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CONDENSATION OF KETONES WITH CYANOACETIC ESTERS. PART I. BENZYLAMINE AND "ETHYLBENZYLAMINE" AS CATALYSTS

By Sukh Dev

The relative effectiveness of ammonium, piperidine, benzylamine and "ethylbenzylamine" acetate as catalysts in the condensation of ketones with ethyl cyanoacetate has been investigated in a qualitative manner. The latter two catalysts have shown special merit.

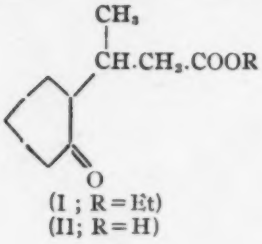
Knoevenagel reaction which embraces the condensation of carbonyl compounds with substances containing an active methylene group in the presence of basic catalysts is of great synthetic value (cf. Migrodichian, "The Chemistry of Organic Cyanogen Compounds", 1947, pp. 319-348). This communication deals with the reaction of ketones with ethyl cyanoacetate.

Unsaturated cyano compounds of the type $RR'C = C(CN)(COOR'')$ have been prepared by the condensation of the carbonyl compounds with cyanoacetic esters in the presence of secondary amines such as piperidine (Harding, Haworth and Perkin, *J. Chem. Soc.*, 1908, **93**, 1943; Haworth and Fyle, *ibid.*, 1914, **105**, 1663; Ingold and Thorpe, *ibid.*, 1919, **115**, 150; Vogel, *ibid.*, 1928, 2010; Barrett and Linstead, *ibid.*, 1935, 436) and diethylamine (Komppa, *Ber.*, 1900, **33**, 3532) as catalysts. Other condensing agents like sodium ethoxide (Haworth *et al.*, *J. Chem. Soc.*, 1909, **95**, 1955, 480; 1908, **93**, 1956), potassium ethoxide (Sörm *et al.*, *Coll. Czech. Chem. Comm.*, 1947, **12**, 251, 554; 1949, **14**, 345) and zinc chloride-aniline complex (Scheiber and Meisel, *Ber.*, 1915, **48**, 238) have also been employed. Soluble amine salts and amides have been shown by Cope (*J. Amer. Chem. Soc.*, 1937, **59**, 2327) to be active agents for such condensations. A significant improvement in carrying out reactions of this type was made when Cope *et al.* (*ibid.*, 1941, **63**, 3452) developed an efficient procedure for the condensation of various ketones with ethyl cyanoacetate; the reaction was simply brought about by refluxing the reactants in an inert solvent like benzene, employing ammonium acetate and acetic acid as catalysts and the water formed was continuously removed by distillation with the inert solvent. Recently Cragoe, Robb and Sprague (*J. Org. Chem.*, 1950, **15**, 38) have described a slight modification of Cope *et. al.*'s procedure (*loc. cit.*), which involves the portionwise addition of ammonium acetate at frequent intervals to the reaction mixture; this method has been found to be effective in bringing about the condensation of highly hindered ketones like camphor and pinacolone (cf. Bagchi and Banerjee, this *Journal*, 1947, **24**, 12). Piperazine has also been employed as a catalyst (Bezzi and Cocco, *Atti ist. Veneto Sci.*, 1948, **106**, 75).

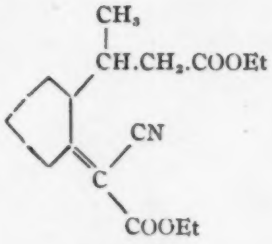
During the course of an investigation* on the synthesis of some degradation products of β-vetivone (Pfau and Plattner, *Helv. Chim. Acta*, 1940, **23**, 768) the condensation

* This work was initiated in 1949.

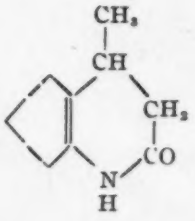
of ethyl cyanoacetate with ethyl *cyclo*pentane-1-oxo-2-β-*n*-butyrate (I) was studied (cf. Bhattacharyya, this *Journal*, 1945, **22**, 214) using the ammonium acetate procedure of Cope *et al.* (*loc. cit.*). Various modifications of the procedure including the use of toluene and xylene as the entrainers and excessive amounts of the catalyst (up to one mole equivalent) were investigated. In all these experiments, none of the desired product (III) could be isolated; but instead, a crystalline compound of composition $C_9H_{13}ON$ was obtained, the yield of which increased with the increasing amounts of the catalyst. It was soon found that the material was solely derived from the condensation of ammonium acetate with the keto-ester. It can be prepared readily by the interaction of molecular proportions of the keto-ester and ammonium acetate with a little acetic acid in boiling benzene, water of the reaction being removed azeotropically. The substance on hydrolysis with 5% aqueous-alcoholic potassium hydroxide gave ammonia and the keto-acid (II); it is also unsaturated to bromine in chloroform. These properties are in good accord with the structure (IV).



(I ; R = Et)
(II; R = H)



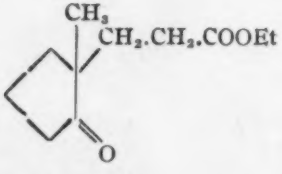
(III)



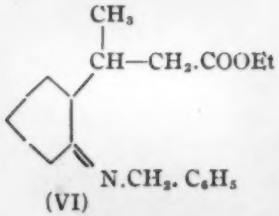
(IV)

Mukharji (*ibid.*, 1947, **24**, 91) has also recorded the formation of a crystalline byproduct during the condensation of ethyl 2-methyl*cyclo*pentanone-2-β-propionate (V) with ethyl cyanoacetate; this byproduct might also be similarly constituted.

Since ammonium acetate was, thus, found to be ineffective for this condensation, piperidine and acetamide were next tried, but were found to be equally useless. It was decided to investigate the action of other amine salts, and in the first instance, benzylamine, which approaches ammonia in its basic strength (benzylamine K_{25}, 2×10^{-5}; ammonium hydroxide K_{25}, 1.8×10^{-5}), was chosen for the study. However, it was soon discovered that benzylamine as well reacted with this keto-ester producing a product, probably (VI).



(V)



(VI)

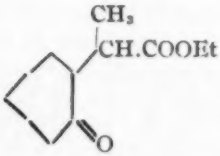
Thus, it is clear that primary amine salts cannot be employed for this particular condensation. Ethylbenzylamine was next investigated. Though the reaction could

not be brought about even by this reagent, these catalysts showed exceptional promise in test experiments with various ketones, and the results obtained so far are described below.

Ammonium acetate, though a very useful catalyst, has certain inherent drawbacks. It is hygroscopic ; during these condensations it slowly undergoes dehydration to acetamide, which may be even carried over with the vapours, and thus during condensations requiring long periods of refluxing, the catalyst spends itself out (cf. Cragoe, Robb and Sprague, *loc. cit.*) and it also may undergo reaction with the condensation product or the starting material, if structurally possible (cf. Cope *et al.*, *loc. cit.*, Cragoe *et al.*, *loc. cit.*, *et seq.*). Another catalyst approaching in its efficiency to ammonium acetate will, thus, be preferrable. Table I shows the results of comparable studies carried out on various ketones ; the results are relative. Ethylbenzylamine used was prepared by the action of ethylbromide on benzylamine (vide Experimental) and may be contaminated with a small percentage of benzylamine.

With these ketones as well as with propiophenone, *p*-methylacetophenone and phenyl-*n*-butyl ketone (all these gave 70-75% of the condensation products with the new catalysts; no comparison with the other catalysts was made), benzylamine and "ethylbenzyl-

TABLE I

No.	Ketone*.	Catalyst**.	Total time §.	Yield.	B.P.	n†.
1	Methyl-*n*-hexyl ketone	Piperidine (A)	18 hrs	89.6%	133-34°/4 mm.	n^{25}, 1.4650
		Am. acetate (B)‡	9	82.0	,,	,,
		Ethylbenzylamine (C)	4½	87.0	,,	,,
		Benzylamine (D)	4	89.0	,,	,,
2	Acetophenone	A	55	74.4	149-50°/2	n^{23}, 1.5430
		B‡	8	63.2	,,	,,
		C	8	74.4	,,	,,
		D	5	75.0	,,	,,
3	*cyclo*Hexanone	B‡	3	83.0	115-16°/3	n^{25}, 1.4950
		C	3	85.0	,,	n^{23}, 1.4960
		D	3	85.0	,,	,, ,,
		A	2-3	3.6	153°/0.2	n^{24}, 1.4825
		B	3	19.3	,,	,, ,,
		C	10	30.0	,,	,, ,,
5	Benzophenone	A	...	...	...	...
		B ‡	15	60	174°/0.2	...
		C	...	...	...	...
		D	13	68.5	174°/0.2 (m.p. 95-96°)	...

* 0.1 *M* of ketone, 0.1 *M* of ethyl cyanoacetate.

** 0.003*M* for the 1st and 3rd ketone; 0.01 *M* for the 2nd, fourth and fifth ketones.

§ Time taken for the separation of water to stop + 1 hr. extra.

† Measurements on once distilled material.

‡ cf. Cope *et al.* (*loc. cit.*).

amine" have been shown to be effective and useful catalysts. These catalysts have also been utilised in the condensation of various keto-esters with ethyl cyanoacetate to yield products required for studies in the azulene and sesquiterpene series (forthcoming publications) and have always been found to be superior to both ammonium acetate and piperidine acetate.

An interesting observation was made when the condensation of benzophenone with ethyl cyanoacetate was attempted in the presence of "ethylbenzylamine". It was found that none of the desired product could be isolated, the starting materials having been recovered. However, under similar conditions ammonium acetate gave a yield of 66% (Cope *et al., loc. cit.*). This difference in the behaviour of "ethylbenzylamine" and ammonium acetate is not readily understandable on the basis of the current reaction mechanism (*Ann. Reports*, 1939, **36**, 210; Watson, *Trans. Faraday Soc.*, 1941, **37**, 707, 718). There is one apparent difference between "ethylbenzylamine" and ammonium acetate; whereas the latter can act as a catalyst *via* ketimines, the former cannot. If this were so, then benzylamine should be an equally effective catalyst for this condensation ; in fact with benzylamine a 68% yield of the condensation product can be obtained. However, a detailed investigation on this point is necessary before any definite views on the reaction mechanism can be outlined.

Since the reaction between a ketone and the cyanoacetic ester is reversible, the action of 2 : 4-dinitrophenylhydrazine reagent on the condensation product should yield the 2:4-dinitrophenylhydrazone of the parent ketone. This, in fact, takes place.

The apparatus shown in Fig. 1 is an improvement over the one in use (Cope *et al., loc.cit.*). In this the condensate is delivered below the surface of the solvent held in the side where the separation of water takes place and thus minimises the chances of any water running back into the reaction vessel. If the returning solvent be allowed to come in contact with a reagent, which will take up the last traces of moisture, the reaction can be pushed to completion much faster. This, in fact, has been realised with the help of the assembly shown in Fig. 2, where the solvent is made to percolate through a bed of activated silica gel before reaching the reaction vessel. With this set up the time of reaction can be reduced by 25-50% of that required, when the assembly No. 1 is used.

Experimental *

Ethylbenzylamine (Pinner and Franz, *Ber.*, 1905, **38**, 1548).—To benzylamine (36 g.) in anhydrous ether (150 c. c.) was added ethyl bromide (36.1 g.) and the mixture was allowed to stand at room temperature (20°-25°) for one week and worked up as usual. The product was purified by distillation, b.p. 188°-193°/684 mm., yield 20 g.

General Procedure for Condensations.—Ethyl cyanoacetate (11.3 g., 0.1 *M*), the ketone (0.1 *M*), acetic acid (3 c.c.), the catalyst (0.033 *M* in the case of reactive ketones and 0.01*M* in the case of less reactive ketones) and dry benzene were placed in a flask and attached to the apparatus shown in Fig. 1.

The mixture was gently refluxed till no more water separated, and then continued for another one hour. It was then cooled, diluted with ether (50 c.c.) and washed

* All m.p. and b.p. uncorrected.

FIG. 1

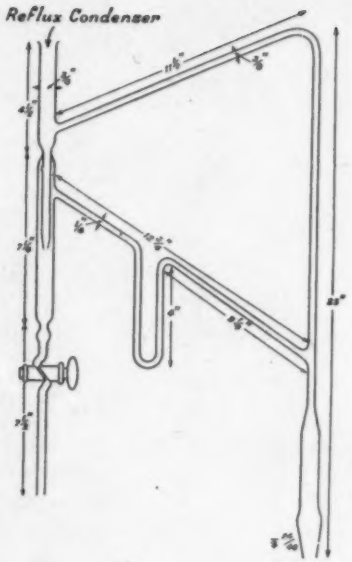
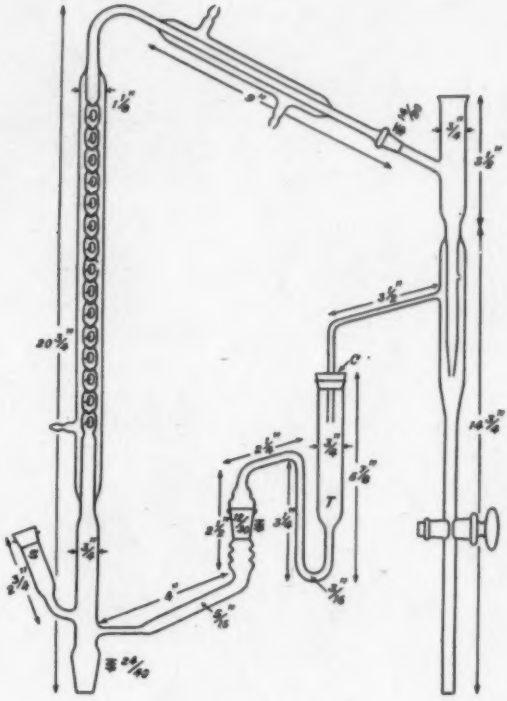


FIG. 2



with water (50 c.c. × 2) and finally with brine (50 c.c.). After drying for several hours over anhydrous Na_2SO_4, the solvents were stripped off and the residue fractionated in vacuum to get the desired condensation product.

Fig. 2 shows the assembly, wherein the returning solvent is made to pass through a bed of activated silica gel (−10, +20 mesh) held in the thimble 'T', between two small plugs of glass wool. By sliding the cork 'C' up or down, the thimble 'T' can be either removed for recharging with the drying agent or held in place. The side-tube 'S' can be used for making any fresh additions of the catalyst. The vigreux column is enclosed in an evacuated jacket.

4-Methyl-5:6-cyclopenteno-3:4-dihydro-2-pyridone (IV?).—A mixture of ethyl *cyclo*pentane-1-oxo-2-*β*-*n*-butyrate (3 g., 0.015*M*) (Bhattacharyya, *loc.cit.*), ammonium acetate (1.8 g., 0.022 *M*), glacial acetic acid (3 c.c.) and benzene (20 c.c.) was refluxed till no more water separated (3 hours). The product was cooled, washed with water and after dyring (Na_2SO_4), the solvent was distilled off. The crystalline residue was recrystallised from light petrol (40°-60°) containing a little benzene in white needles, m.p. 123-25°, yield, 1.5 g. (Found: C, 71.2; H, 8.8; N, 9.3. $C_9H_{13}ON$ requires C, 71.5; H, 8.6; N, 9.2 per cent).

The compound can be readily distilled from a sausage flask (b.p. 140°-150°/2 mm.) and easily sublimes at 100°/1 mm. If in the above reaction the acid (II) instead of the ester (I) is employed, the same product is isolated.

The reaction mixture after *hydrolysis* of the pyridone (2.0 g.) by refluxing with aqueous-alcoholic potassium hydroxide (5%, 30 c. c.) was cooled, diluted with water, extracted with ether to remove the neutral portion and then acidified with concentrated hydrochloric acid. The liberated acid after purification by ether extraction, washing and drying distilled at 145-49°/3 mm., yield 1.2 g. This was directly converted into the 2:4-*dinitrophenylhydrazone* of its ethyl ester (H_2SO_4 method). The product was repeatedly crystallised from ethyl alcohol to give light orange plates, m.p. 106.5°–107.5°; mixed m.p. with an authentic sample remained the same. (Found: N, 14.9. Calc. for $C_{17}H_{22}O_6N_4$: N, 14.8 per cent).

Benzylamine Condensation Product (VI).—The keto-ester (9.9 g., 0.05 *M*), benzylamine (5.36 g., 0.05 *M*), acetic acid (1 c.c.) and anhydrous benzene (30 c.c.) were gently refluxed till no more water separated (4½ hours) and then worked up as usual. It is a colorless, viscous liquid, b.p. 160°/0.65 mm., yield 11.5 g., n^{26}, 1.5625, d_4^{26}, 1.094 ; M_D, 85.11 (calc. for structure VI, M_D, 84.88). (Found: C, 75.6; H, 8.3. $C_{18}H_{25}O_2N$ requires C, 75.2; H, 8.9 per cent).

Action of 2:4-DNP Reagent on Ethyl Cyanoacetate Condensation Product.—The following experiment is described as a representative of the general reaction:

The condensation product from acetophenone (0.01*M*) was added to a solution of 2:4-dinitrophenylhydrazine (1.98 g., 0.01*M*) in 3 c.c. of concentrated sulphuric acid, alcohol (25 c.c., 95%) and water (10 c. c.). The mixture was refluxed for 30 hours and the bright red precipitate filtered off after cooling; yield quantitative, m.p. 238-40°. It was recrystallised from acetic acid, m.p. 249-50° (Campbell, *Analyst*, 1936, **61**, 393 gives m.p. 249-50°).

The author wishes to record his thanks to Prof. A. C. Cope (M. I. T., U. S. A.) for the interest he has shown in the investigation. Thanks are also due to Mr. D.P.Bose for the fabrication of the assemblies shown.

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PRODUCTION OF JOSHI EFFECT IN AIR IN PRESENCE OF ORGANIC VAPOURS UNDER X-RAYS

By G. V. Asolkar

The significant finding that on addition of traces of organic liquids (e.g. benzene, toluene, xylene, *cyclo*hexane, carbon tetrachloride, acetone etc.) Joshi effect ($\pm\Delta i$) under X-rays is developed in air-organic vapour mixture at *atmospheric pressure* which is otherwise absent in air alone at the same pressure, is now reported. Thus, air-benzene mixture at atmospheric pressure with X-rays of 2.5 mA tube current and 23.2 kilovolts anode voltage showed +100% positive Joshi effect at 10.0 kV exciting potential. As the exciting potential (V) was increased, the $+\Delta i$ changed sign at about 11.0 kV and gave −22% negative Joshi effect. With further increase in V, $-\%\Delta i$ decreased to 5 at 20.0 kV. Thus $-\%\Delta i$ was maximum at the threshold potential V_s and decreased with $(V-V_s)$. Positive Joshi effect was observed at potentials just below V_s. Essentially similar results were obtained with other air-organic vapour mixtures.

The magnitude of $\pm\Delta i$ depends *inter alia* on (*i*) frequency and intensity of X-ray beam, (*ii*) nature of the organic vapour in air, (*iii*) the interelectrode distance and (*iv*) 'ageing'.

The results are explained by an extention of Joshi's theory, associating $-\Delta i$ with the space charge effect due to negative ions, to a consideration of the choking action of the positive ionic space charge. The relation $i=Q/(t_a+t_m)$ is examined for the changes in the discharge current under X-ray irradiation.

Review of literature shows that even in chlorine, which is particularly adapted for the production of the above phenomenon $\pm\Delta i$, its value is only a few per cent at 60 cm. Hg pressure, and decreases thereafter (Joshi, *Nature*, 1944, **153**, 434). In air $-\Delta i$ was found only at a much smaller pressure of about a few cm. Hg (Vishvanathan and Rao, *Proc. Ind. Acad. Sci.*, 1949, **29A**, 98; Rao, *ibid.*, 1948, **27A**, 72). During studies of the above phenomenon, reported earlier (this *Journal*, 1953, **30**, 233, 241)*, the observation was made that introduction of but a small proportion of organic vapour in air even at atmospheric pressure induced a pronounced Joshi effect under X-ray irradiation.

This has significance *inter alia* from the standpoint on Joshi's observation that *ceteris paribus* $+\Delta i$ is favoured by polyatomicals. It was considered desirable therefore to obtain more information about this role of organic vapours.

Experimental

The general experimental set up and procedure has been described in earlier communications (Asolkar, *loc. cit.*). Carefully cleaned glass ozonisers of various interelectrode distances were employed; in such a series, the diameter of the outer electrode was constant. The annular space of the ozoniser contained air at atmospheric pressure and temperature. A drop of the liquid, e. g. benzene, was next introduced in the annular space. After sometime, when the vapour-air mixture attained a dynamic equilibrium, the system was excited by a transformer discharge, and $\pm\Delta i$ due to X-rays of various intensities and frequencies were determined as described earlier. The results are shown in Tables I to V.

*See also Proc. Ind. Sci. Cong., 1952, *Chem. Sec.*, Abst. No, 71.

TABLE I

Potential variation of Joshi effect in air - organic vapour mixture under X-rays.
Hardness (anode voltage) = 23.2 kilovolts. Intensity (anode current) = 2.5 mA.
Interelectrode distance = 4 mm.

Air—benzene mixture.					Air—toluene mixture.					Air—xylene mixture.				
Exciting potential in kV.	Current in dark, i_D.	Current under X-rays, i_L.	Δi.	$\%\Delta i$.	kV.	i_D.	i_L.	Δi.	$\%\Delta i$.	kV.	i_D.	i_L.	Δi.	$\%\Delta i$
8.0	8	8	0	0						8.0	8	10	+ 2	+25
8.4	9	9	0	0						8.5	10	20	+10	+100
8 8	10	11	+ 1	+ 10	9	20	20	0	0	9.0	12	20	+ 8	+67
9.2	12	14	+ 2	+ 17	10	34	50	+16	+47	10.0	14	22	+ 8	+57
9.6	18	30	+12	+ 67	11	55	60	+ 5	+ 9	11.0	20	22	+ 2	+10
10.0	22	44	+22	+100	12	70	62	− 8	−11	12.0	48	40	− 8	−17
10.4	30	44	+14	+ 47	13	78	69	− 9	−12	13.0	68	59	− 9	−13
11.0	59	46	−13	− 22	14	87	79	− 8	− 9	14.0	87	77	−10	−12
12.0	70	63	− 7	− 10	15	94	87	− 7	− 7	15.0	105	95	−10	−10
13.0	78	70	− 8	− 10	16	100	94	− 6	− 6	16.0	122	111	−11	− 9
14.0	85	75	−10	− 12	17	106	100	− 6	− 6	17.0	139	128	−11	− 8
15.0	96	86	−10	− 10	18	112	107	− 5	− 4	18.0	156	144	−12	− 6
16.0	100	90	−10	− 10	19	121	117	− 4	− 3	19.0	173	162	−11	− 6
17.0	110	100	−10	− 9	20	129	125	− 4	− 3	20.0	190	180	−10	− 5
18.0	118	108	−10	− 9										
19.0	130	121	− 9	− 7										
20.0	142	135	− 7	− 5										

Air—*cyclo*hexane.					Air—carbon tetrachloride.					Air—acetone.				
kV.	i_D.	i_L.	Δi.	$\%\Delta i$.	kV.	i_D.	i_L.	Δi.	$\%\Delta i$.	kV.	i_D.	i_L.	Δi.	$\%\Delta i$.
8.0	3	3	0	0	8.0	5	5	0	0					
8.5	5	6	+ 1	+20	8.5	12	18	+6	+50					
9.0	7	12	+ 5	+71	9.0	20	42	+22	+110	9.0	7	7	0	0
9.5	10	20	+10	+100	9.5	38	47	+9	+24	9.5	12	40	+28	+233
10.0	32	27	− 5	−16	10.0	65	55	−10	−15	10.0	32	45	+13	+41
11.0	51	45	− 6	−11	11.0	77	66	−11	−14	11.0	54	47	− 7	−13
12.0	69	60	− 9	−13	12.0	85	75	−10	−12	12.0	69	62	− 7	−10
13.0	83	73	−10	−12	13.0	91	80	−11	−12	13.0	79	72	− 7	− 9
14.0	94	83	−11	−12	14.0	95	85	−10	−11	14.0	89	83	− 6	− 7
15.0	106	95	−11	−10	15.0	104	93	−11	−11	15.0	97	91	− 6	− 6
16.0	116	105	−11	−10	16.0	108	96	−12	−11	16.0	107	101	− 6	− 6
17.0	126	115	−11	− 9	17.0	112	100	−12	−11	17.0	116	110	− 6	− 5
18.0	135	125	−10	− 7	18.0	120	107	−13	−11	18.0	123	118	− 5	− 4
19.0	149	140	− 9	− 6	19.0	127	115	−12	− 9	19.0	132	128	− 4	− 3
20.0	159	151	− 8	− 5	20.0	131	121	−10	− 8	20.0	137	134	− 3	− 2

TABLE II

Intensity variation of positive Joshi effect in air—xylene mixture under X-rays.
Anode voltage = 23.2 kilovolts. Interelectrode distance = 4m.

Intensity (anode current in mA).	Exciting potential. 8kV Current in dark i_D=8			10kV i_D=15			11.5kV i_D=32		
	i_L.	$+\Delta i$.	$+\%\Delta i$.	i_L.	$+\Delta i$	$+\%\Delta i$.	i_L.	$+\Delta i$	$+\%\Delta i$.
0.50	9	1	11	18	3	20	34	+2	+6
2.0	10	2	25	19	4	26	35	+3	+9
3.0	11	3	37	22	7	46	33	+1	+3
5.5	10	2	25	17	2	13	30	−2	−6

Intensity variation of negative Joshi effect in air—organic vapour mixtures.

	Air—benzene 16kV i_D=100			Air—toluene 12kV i_D=70			Air—xylene 12kV i_D=48		
	i_L.	$-\Delta i$.	$-\%\Delta i$.	i_L.	$-\Delta i$	$-\%\Delta i$.	i_L.	$-\Delta i$.	$-\%\Delta i$.
0.5	96	4	4	66	4	6	45	3	6
1.0	94	6	6	64	6	9	43	5	10
1.5	92	8	8	62	8	11	41	7	15
2.0	91	9	9	63	7	10	39	9	19
2.5	90	10	10	64	6	9	40	8	17
3.0	92	8	8	64	6	9	40	8	17
3.5	92	8	8	65	5	7	41	7	15
4.0	93	7	7	66	4	6	43	5	10
5.0	94	6	6	—	—	—	45	3	6
5.5	95	5	5	67	3	4	46	2	4

TABLE III

Frequency (hardness) variation of negative Joshi effect in air—organic vapour mixture under X-rays.
Anode current = 2.5 mA.

Anode voltage (kilovolts).	Air—benzene 16kV i_D=100			Air—toluene 12kV i_D=70			Air—xylene 12kV i_D=48		
	i_L	$-\Delta i$	$-\%\Delta i$	i_L	$-\Delta i$	$-\%\Delta i$	i_L	$-\Delta i$	$-\%\Delta i$
10.8	96	4	4	67	3	4	46	2	4
13.9	93	7	7	65	5	7	44	4	8
17.0	91	9	9	64	6	9	42	5	10
20.1	90	10	10	63	7	10	41	7	15
23.2	90	10	10	62	8	11	40	8	17

TABLE IV

Influence of interelectrode distance on Joshi effect in air—benzene mixture under X-rays. Intensity = 2.5 mA (anode current). Frequency = 23.2 kilovolts (anode voltage). Exciting potential = 12 kV.

Interelectrode distance (d).	i_D.	i_L.	$-\Delta i$.	$-\%\Delta i$	Interelectrode distance (d).	i_D.	i_L.	$-\Delta i$	$-\%\Delta i$
2 mm.	67	53	14	20	7 mm.	101	83	18	18
4	68	53	15	22	8	103	89	14	14
6	80	61	19	24	9	104	99	5	5

TABLE V

Influence of ageing under discharge on Joshi effect in air—benzene mixture under X-rays. Hardness (anode voltage) = 23.2 kilovolts. Intensity (anode current) = 2 5 mA. Temp. = 27°.

	Time = 0 min.				Time = 10 min.				Time = 20 min.			
kV.	i_D.	i_L.	Δi.	$\%\Delta i$.	i_D.	i_L.	Δi.	$\%\Delta i$.	i_D.	i_L.	Δi.	$\%\Delta i$.
8	8	13	+ 5	+63	6	8	+ 2	+33	6	7	+1	+17
10	74	63	−11	−15	72	61	−11	−15	68	58	−10	−15
12	83	78	−10	−11	84	74	−10	−12	85	75	−10	−12
14	104	94	−10	−10	102	92	−10	−10	103	93	−10	−10
16	121	111	−10	− 8	118	108	−10	− 8	115	105	−10	− 9
18	145	138	− 7	− 5	139	131	− 8	− 6	140	132	− 8	− 6
20	155	150	− 5	− 3	151	145	− 6	− 4	144	137	− 7	− 5

	Time = 30 mins.				Time = 40 mins.			
kV.	i_D.	i_L.	Δi.	$\%\Delta i$.	i_D.	i_L.	Δi.	$\%\Delta i$.
8	4	4	0	0	0	0	0	0
10	70	59	−11	−16	71	60	−11	−16
12	79	68	−11	−14	82	71	−11	−13
14	99	88	−11	−11	100	89	−11	−11
16	110	100	−10	− 9	110	100	−10	− 9
18	132	124	− 8	− 6	131	122	− 9	− 7
20	142	134	− 8	− 6	143	136	− 7	− 5

The discharge current i was measured with a galvanometer actuated by a diode coupled resistively with the L. T. of the ozoniser. The wave form of the current was observed in dark and under X-ray irradiation using a cathode ray oscillograph (Du Mont 208B). Values of $\pm\Delta i$ were obtained as a function of the nature of vapours introduced and 'ageing' under discharge with various intensities and frequencies of X-rays.

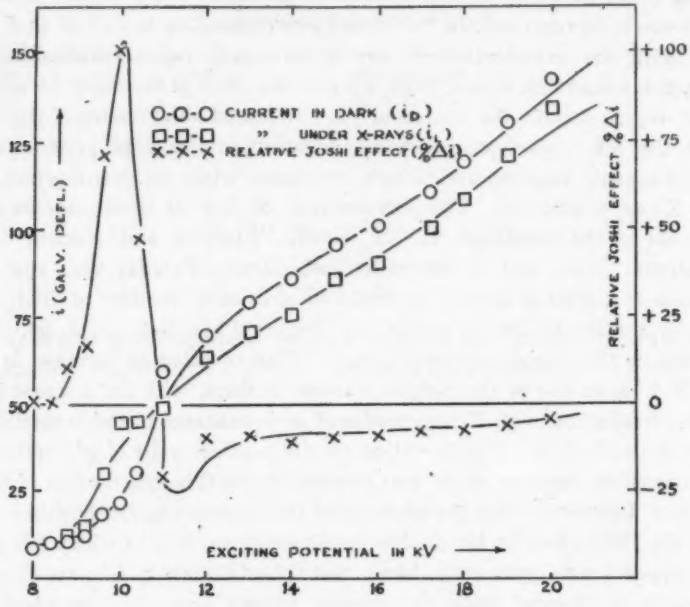
DISCUSSION

Joshi effect ($\pm\Delta i$) is unobserved in air alone despite a wide range of variation of the exciting potential kV (8-20), interelectrode distance, d (2-9 mm.), the intensity, I (0.5 to 6 mA anode current) and the hardness (ν, corresponding to 10.8 to 23.2 kilovolts) of X-rays. With the introduction of any of the organic vapours studied (see Table I) e.g. benzene, it is found that at first there is a positive effect of the order 16-100% in the low potential region below the threshold V_m. Repeated observations of the wave form showed that the h.f. pulses indicative of a 'continuous discharge' present prior to the introduction of organic vapours, and which continued after its introduction, were not affected by X-ray irradiation. The introduction of any of these vapours produces a sensible decrease of the threshold V_m (cf. Korff, "Electron and Nuclear Counters", D. Van Nostrand, 1946) and as shown by Joshi (*Trans. Faraday Soc.*, 1929, **25**, 108, 118) an increase of i; what is more, it produces an additional number of high frequency pulses (h. f.'s) similar to Trichel pulses (cf. Trichel, *Phys. Rev.*, 1938, **54**, 1078; 1939, **55**, 382) as seen on the cathode ray oscillograph. This revealed an increase in the total number of h. f.' s, as also of the height of some of them, with the increase in exciting potential kV. Irradiation with X-rays produced an instantaneous and reversible *decrease* in the height of the h. f.' s. The formation on the ozoniser walls of adsorption layer (s) of these condensible vapours is in part responsible for this sensitisation of the system. It is suggested tentatively that the presence of the organic vapour sensitises the system in respect of the Joshi effect by the production of additional h. f.' s which are affected by X-rays. It appears also extremely likely that the *additional* h. f.' s are those observed when the system is charged with the organic vapour alone, *i.e.*, in absence of air. Work is in progress to obtain more detailed information on this point by analysing the h. f.' s with filter circuits. With the introduction of the organic vapours it is found that at first there is a *positive* effect in the low potential region below the threshold V_m. This *positive* effect first tends to increase with increase in applied kV. Thus e.g. in benzene vapour, the interelectrode distance being 4 mm., the *positive* effect increases from 10 to 100% as the potential is raised from 8.8 to 10.0 kV. This may well be associated with the potential amplification of the current caused primarily by the photoelectric effect under X-rays. This is characterised by a reversible appearance of h.f. pulses as viewed with the oscillograph.

These results also confirm the generality of the finding in this field of work that the *positive* effect (which is to be anticipated in excited media and particularly under X-rays) is restricted to a remarkably narrow range of operative conditions, e.g. the exciting potential, compared with the negative effect (see Fig. 1). It is, however, instructive to point out that, e. g. in xylene—air mixture (see Table II), the *positive* effect at 10.0 kV varies in the range 20-46%, although the intensity is increased from 0.5 to 5.5 mA anode current. At the higher exciting voltage (11.5 kV) the effect is reduced; it however, decreases from +6% to −6% in the same intensity range. It is suggestive that near V_m, the smaller $+\Delta i$ changes sign as a result of the above tenfold increase of intensity. This also implies that photoelectric ionisation is not the sole determinant of $+\Delta i$.

FIG. 1

Potential variation of Joshi effect in air—benzene mixture under X-rays.



That an additional factor is involved in this action of X-rays is suggested by the fact that with but a further small increase of the applied kV, the *positive* effect not only diminishes in magnitude but changes sign to give the *negative* effect $-\Delta i$. The *negative* effect is maximum near V_m and decreases with the overvoltage $V-V_m$, a result in accord with the general finding for this phenomenon in the visible and ultra-violet (see Table I and Fig. 1) (Joshi, *loc.cit. Curr. Sci.*, 1945, **14**, 317).

It is instructive to consider at constant hardness (ν) the influence of an increase of intensity on the *negative* Joshi effect in the above mixtures. It is generally found that $-\%\Delta i$ increases (numerically) to a maximum and then diminishes. Thus, e. g. in air − benzene mixture at 16 kV, $-\%\Delta i$ increases from 4 for intensity 0.5 mA anode current, increasing to a maximum of 10% at 2 mA and then gradually declining to 8% at 3 mA and 5% at 5.5 mA anode current (see Table II). It is seen that for a given hardness of X-rays, the optimum intensity corresponding to the production of maximum $-\%\Delta i$ is independent of the applied potential. It lies within 2 to 2.5 mA for benzene—air, toluene—air and xylene—air mixtures (see Table II). This value of optimum intensity is practically the same as that when pure and unmixed vapours are employed, which is to be anticipated since the X-ray sensitive h. f. 's are not observed in pure air; they occur only on the introduction of the organic vapour, when alone the system shows $\pm\Delta i$, in the potential range studied.

Earlier during this work, the non-linearity of $-\%\Delta i$—I curves was emphasised by Joshi (*Nature*, 1913, **151**, 561) to be in striking contrast with the metal-in-vacuo photoelectric effect. In various spectral regions of the visible and ultraviolet $-\%\Delta i - I$ curves rise to a flat maximum indicative of saturation (Joshi, *Curr. Sci.*, 1945, **14**, 35). Results of Deo (*Indian J. Phys.*, 1944, **18**, 83) show that the tendency to saturation sets in earlier, the greater the wave-length of the radiation employed to cause $-\Delta i$; or in other words, the concavity towards the intensity axis, observed by Joshi to be a general characteristic of $-\Delta i$, increases with ν. This feature is shown by the foregoing $-\%\Delta i$—I results under X-rays. The characteristic additional feature observed under the X-rays, viz., the numerical decrease of $-\%\Delta i$ after the maximum, is in accord with much greater concavity to I-axis due to the much greater frequency ν of X-rays than the visible or ultraviolet (see Table II).

The results at various constant intensities for the influence of frequency ν on $-\%\Delta i$ in the above mixtures reveal linearity except in the region of large frequency when a tendency to saturation is noticed (see Table III).

The influence of the interelectrode distance, d, which determines the field intensity in the discharge space (all other factors being constant), was next studied. Observations were made at $d = 2, 4, 6, 7, 8, 9$ mm. It was found, e. g. in benzene—air mixture, excited at 16kV, that the maximum $-\%\Delta i$ for above values of d were respectively 20, 22, 24, 18, 14 and 5 (see Table IV). The results for toluene were closely similar. As was to be expected, the proportion of the h.f. pulses prior to irradiation was maximum at $d = 6$ mm., where $-\%\Delta i$ was also maximum. At large values for d, $-\%\Delta i$ was negligible; and as suggested by the very low current and scarcity of h.f. pulses on the cathode ray oscillograph.

The fundamental importance of 'ageing' the system under discharge on the inception, maximisation and change of sign of Δi even in elementary gases was emphasised by Joshi early during this work (Joshi, *loc. cit.* Deo, *Proc. Ind. Acad. Sci.*, 1945, **21A**, 76). This ageing effect has been associated with the formation of an adsorption layer on the ozoniser walls consisting besides normal particles from the gas phase, of the excited and ionic species produced under the discharge. It is known that $+\Delta i$ sets in at less than, or very near the threshold potential V_m where the discharge is just incipient and intermittent. The discharge becomes 'continuous' in the next higher potential region causing $-\Delta i$. The latter decreases rapidly as the applied kV is further increased. Despite the comparatively low potential employed in the production of $\pm\Delta i$, the possible decomposition is an additional factor in the influence of ageing, especially of a compound vapour. It was found that the positive effect in the case of above organic vapour mixiure was reduced very markedly (and became negligible in the majority of them) by but short durations of ageing of about 30 minutes (see Table V). During this period the *negative* Joshi effect (in the appropriate potential region) increased by about 1-2%; the corresponding discharge current decreased by about 10% and was rendered stabler. Precisely similar results were observed by Goyal (this *Jonrnal*, 1947, **24**, 203 ; cf. Mallikarjunappa, *ibid.*, 1948, **25**, 197; Mohonty, *ibid.*, 1951, **28**, 487) that a preliminary ageing under the discharge of about the above period reduced

and steadied markedly the discharge but increased the associated *negative* effect in chlorine and ascribed it to the formation of an electrode layer, the photoelectric emission from which under the external radiation is fundamental to the production of the above effect (Joshi, *Curr. Sci.*, 1947, **16**, 19).

The generality of these results receives explanation on an extension to the role of positive ions of Joshi's theory of current decrease due to space charge by negative ion formation (Joshi, *loc. cit.*) under discharge. In the present instance, besides negative ions due to the well known high electron affinity of the free radicals, it is suggested that the accumulation of the positive ions left behind by the photoelectrons causing Townsend avalanches inhibits the current to give $-\Delta i$ (cf. Asolkar, *loc. cit.*). Montgomery and Montgomery (*Phys. Rev.*, 1940, **51**, 1030) found that $i=Q/(t_a+t_m)$ (cf. Asolkar, this *Journal*, 1953, **30**, 248). Irradiation during active time 't_a' produces an additional positive ion space charge between the cathode and the normal space charge. This reduces the field and decreases electronic charge Q and therefore, the pulse height. The relaxation time 't_m' is also increased because of the screening action of the additional space charge. Both these factors decrease i to give $-\Delta i$. It is also shown that on this view the small height, 'satellite' pulses should increase in number simultaneously with the production of $+\Delta i$, which was first observed by Jatar (*J. Sci. Ind. Res.*, 1950, **9B**, 283) and by the author (*loc. cit.*) as also during the present work.

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CHEMICAL INVESTIGATION OF INDIAN MEDICINAL PLANTS. PART I. INVESTIGATION OF *SWERTIA DECUSSATA*: ISOLATION OF DECUSSATIN AND SWERTININ

By Miss S. R. Dalal, Suresh Sethna[1] and R. C. Shah[2]

Swertia decussata, a plant which is used as an excellent substitute for *chiratta*, has been chemically investigated. The flowers, stems and roots have been extracted separately with different solvents. From the petroleum ether extract of the flowers a yellow substance (m.p. 149-50°, $C_{16}H_{14}O_6$) has been isolated. It has been named Decussatin. From the sulphuric ether extract an acid has been obtained which is found to be the known oleanolic acid. The ether extract of the stems gave a yellow crystalline product (m.p. 217°, $C_{15}H_{12}O_6$), which has been named Swertinin. The ash obtained from the flowers has been qualitatively and quantitatively analysed. The alcoholic extracts of the flowers, the stems and the roots were very bitter in taste but the bitter principle could not be isolated in a pure state.

The Natural Order Gentianaceae contains various plants of medicinal importance. Many plants belonging to this Order are indigenous to India. These plants are extensively used as bitter tonics and febrifuges in the Ayurvedic system of medicine. The present work deals with the chemical investigation of *Swertia decussata*, a plant which is used as an excellent substitute for *Swertia chiratta* in Western India and which grows wild all over the Western Ghats. It is a small plant which flowers from October to January. The flowers are white and numerous. For the present investigation the plant was collected at Bhilad near Panchgani in the Western Ghats and was identified by Rev. Fr. Santapau, Head of the Botany Department, St. Xavier's College, Bombay.

The flowers, stems and roots were extracted separately with different solvents in the cold.

From the petroleum ether extract of the sun-dried, powdered flower a yellow substance, m.p. 149-50°, was obtained. This product has been named *Decussatin*. From the sulphuric ether extract an acid of m.p. 304°-306° was obtained. It gave an acetyl derivative, m.p. 256°. It gave all the colour reactions of the triterpenoid derivative, oleanolic acid.

The absolute alcohol extract of the flowers gave no definite product. The hydrochloric acid extract gave positive tests with alkaloidal reagents, but no alkaloid could be isolated.

From the ether extract of the sun-dried, powdered stems a light yellow amorphous mass was obtained (m.p. 217°) which has been named *Swertinin*. The ether extract of the same also gave oleanolic acid, a white compound (m.p. 234°) and an oil. The last two were not enough for further investigation. The alcohol extract gave a brown resinous mass which was extremely bitter in taste, but attempts to get a definite product from this were unsuccessful. On hydrolysis, only a small quantity of swertinin was obtained. Extraction of stems with acetone and 1% hydrochloric acid gave nothing.

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The sun-dried roots on extraction with petroleum ether gave a small quantity of decussatin. The sulphuric ether extract gave nothing. The alcoholic extract gave a bitter resinous mass form which no pure product could be isolated. No definite product could be isolated from the petroleum ether extract of the stems.

Decussatin and Swertinin.—Decussatin analysed for $C_{16}H_{14}O_6$. Its acetyl derivative analysed for $C_{18}H_{16}O_7$, and the methyl ether for $C_{17}H_{16}O_6$, indicating that one hydroxyl group was acetylated and methylated. Zeisel's determination indicated the presence of three methoxyl groups.

Swertinin analysed for $C_{15}H_{12}O_6$, the acetyl and methoxy derivatives analysed for $C_{19}H_{16}O_8$, and $C_{17}H_{16}O_6$ respectively, indicating that two hydroxyl groups were acetylated and methylated. Partial methylation of swertinin gave decussatin. Zeisel's determination indicated the presence of two methoxyl groups in swertinin. Work on the structures of swertinin and decussatin will form the subject matter of Part II of this series.

EXPERIMENTAL

Extraction of Flowers

Extraction with Petroleum Ether: Isolation of Decussatin.—Powdered, sun-dried flowers (1.5 kg.) were repeatedly extracted by completely soaking them in petroleum ether (b.p. range 40°-60°, 10 litres) for 24 hours each time. The extracts on concentration and cooling in ice afforded yellow needles which were filtered off. The yellow needles (1.5 g.) were refluxed with a little petroleum ether to remove a waxy material and finally crystallised from alcohol in deep yellow needles, m.p. 149-50°. This product has been named *Decussatin*.

The residue obtained on removal of the petroleum ether under reduced pressure from the concentrated extract was a greenish pasty mass (25 g.) which was dissolved in sulphuric ether and successively extracted with sodium bicarbonate, sodium hydroxide, and dilute hydrochloric acid, but no definite product could be isolated from these extracts. The ethereal layer after the above extractions and distillation of the ether gave an orange coloured oil which was not enough for further work.

Decussatin.—Decussatin is soluble in chloroform, alcohol and acetone; sparingly soluble in benzene, petroleum ether and sulphuric ether; insoluble in water and in dilute hydrochloric acid. With sodium and potassium hydroxide it forms sparingly soluble sodium and potassium salts. [Found: C, 63.5; 63.5; H, 4.3; 4.5; OCH_3, 28.1; 28.1; M.W. (Rast), 288.8; 288.6. $C_{16}H_{14}O_6$ requires C, 63.6; H, 4.6; 3 OCH_3, 31.0 per cent. M.W., 302]. The results of methoxyl determination are slightly lower probably due to estimations having been carried out with *d* 1.7 hydriodic acid as *d* 1.9 hydriodic acid was not available. For more than two methoxyl groups the latter is generally required (cf. Niederl and Niederl, "Organic Quantitative Micro-analysis", 1946, p. 248).

The *acetyl derivative*, prepared by heating decussatin (0.1 g.) with acetic anhydride (2 c.c.) and a drop of pyridine on a steam-bath for 6 hours, was crystallised from alcohol in white needles, m.p. 167°. It gives no coloration with alcoholic ferric chloride. (Found: C, 62.7; H, 4.5. $C_{18}H_{16}O_7$ requires C, 62.8; H, 4.6 per cent).

The *methyl ether*, prepared by refluxing decussatin (0.1 g.) in dry acetone (20 c.c.) with methyl iodide (3 c.c.) and potassium carbonate (0.5 g.) on a steam-bath for 24 hours, was crystallised from rectified spirit in pale yellow plates, m.p. 165°. It gives no coloration with alcoholic ferric chloride. (Found : C, 58.2, 58.5; H, 5.9, 5.9. $C_{17}H_{16}O_6$, $2H_2O$ requires C, 58 3; H, 5.7 per cent). [Found (sample, dried at 120° for 6 hours under reduced pressure) : C, 64.0; H, 5.0. $C_{17}H_{16}O_6$ requires C, 64.5 ; H, 5.1 per cent].

The same methyl ether was obtained on methylation in acetone solution with dimethyl sulphate and alkali at room temperature.

Extraction with Sulphuric Ether : Isolation of Oleanolic Acid.—The dried flowers after extraction with petroleum ether were repeatedly extracted with ether (10 litres) in the cold by keeping overnight. The ethereal extracts on concentration gave a greenish pasty mass (24 g.) which was redissolved in minimum quantity of ether, and successively extracted with sodium bicarbonate, sodium hydroxide and dilute hydrochloric acid.

No definite product could be isolated from the sodium bicarbonate extract. From the sodium hydroxide extract on acidification a small quantity of a white substance of m.p. 223° was obtained which could not be worked up further for the paucity of sufficient material.

During extraction with sodium bicarbonate and sodium hydroxide, an interstitial layer of suspended solid was formed which was filtered off. This precipitate was washed with boiling water, and the residue, insoluble in hot water, was ground with concentrated hydrochloric acid and extracted with ether. The extract was dried over anhydrous sodium sulphate and the ether distilled off. This gave a light green solid (4.8 g.), m.p. 286-90°. This was repeatedly crystallised from alcohol (charcoal) when white needles were obtained, m.p. 304-306°. This substance was found to be oleanolic acid (described later) ; m.p. given in the literature, 310° (corr.) (cf. Elsevier, "Encyclopaedia of Organic Compounds", 1940, Vol. 14, Series iii, p. 359).

Nothing was obtained from the hydrochloric acid extract. The original ether extract after the above extractions gave a light brown-coloured oil which was not sufficient for further work.

Oleanolic Acid.—The substance of m.p. 304-306°, obtained above, is very soluble in alcohol, methanol, chloroform and acetic acid; sparingly soluble in ether, petroleum ether and ethyl acetate and insoluble in water. It gave a sparingly soluble sodium salt with sodium bicarbonate and sodium hydroxide. It absorbed bromine in chloroform and decolorised alkaline potassium permanganate. It gave no coloration with alcoholic ferric chloride ; it gave an orange coloration with concentrated sulphuric acid and a red coloration with chloroform and concentrated sulphuric acid, the red colour changing to green through blue with acetic anhydride and concentrated sulphuric acid. [Found (sample, dried at 140° under reduced pressure) : C, 77.8 ; 77.9 ; H, 10.3 ; 10.4. Calc. for $C_{30}H_{48}O_3$: C, 78.9 ; H, 10.5 per cent]. Mixed m.p. with oleanolic acid (m.p. 310°), obtained from the sodium salt of oleanolic acid and also by hydrolysis of the acetyl derivative of oleanolic and kindly supplied by Prof. Jones and Dr. Halsall, was not depressed. The acetyl derivative was prepared by heating the acid (0.2 g.) with acetic anhydride (2 c.c.) and a drop of pyridine on a steam-

bath for 6 hours. The product obtained on pouring the reaction mixture in water containing a few drops of dilute hydrochloric acid was crystallised from alcohol in needles, m.p. 256°. Mixed melting point with the acetyl derivative of oleanolic acid (m.p. 264°-65°), kindly supplied by Professor Jones and Dr. Halsall, was not depressed. (Found : C, 76.7; 76.3; H, 9.6, 9.9. Calc. for $C_{32}H_{50}O_4$: C, 77.1; H, 10.0 per cent).

Extraction with Absolute Alcohol.—The flowers were next extracted repeatedly with cold alcohol. The alcohol was removed under reduced pressure when a dark brown resinous mass (50 g.) was obtained. This dissolved completely in water. The aqueous solution was extracted with chloroform and ethyl acetate, and then treated with lead acetate and basic lead acetate, but no pure product could be obtained in any of these treatments.

Extraction with 1% Hydrochloric Acid.—The flowers were next extracted with 1% cold hydrochloric acid. The extract was tested with alkaloidal reagents like phosphomolybdic acid, potassium mercuric iodide and phosphotungstic acid when positive results were obtained ; so the total extract was made alkaline with ammonia when a gelatinous precipitate was obtained. The mass was extracted with ether and chloroform. Both these extracts left a thick orange-coloured semi-solid (0.1 g.) which gave precipitate with potassium mercuric iodide.

The ammoniacal solution containing the precipitate was filtered. The dark brown precipitate (14 g.) was inorganic matter, and qualitative analysis showed the presence of iron, aluminium and phosphate ions. The filtrate was treated with lead acetate and basic lead acetate, but no definite product was obtained.

Extraction of Stems

Extraction with Petroleum Ether.—Sun-dried, powdered stems (3 kg.) were repeatedly extracted by soaking in petroleum ether (b.p. range 40°-60°, 10 litres) for 24 hours every time. The extracts on removal of the petroleum ether left a greenish pasty mass (4 g.) which could not be purified further.

Extraction with Sulphuric Ether: Isolation of Swertinin.—The stems from above were repeatedly extracted with sulphuric ether (10 litres) by keeping overnight. A light yellow, amorphous, sticky mass (approx. 35 g.) was left on removal of the solvent. This was treated with ether (2 litres) when all except approximately 5 g. dissolved. The insoluble portion was crystallised first from alcohol-acetone mixture and finally from alcohol-chloroform mixture when deep yellow needles, m.p. 217°, were obtained. This product is named *Swertinin*.

The ethereal solution was successively extracted with sodium bicarbonate, sodium hydroxide and dilute hydrochloric acid. The sodium hydroxide extract on acidification and ether extraction gave a solid product which on treatment with charcoal and final crystallisation from alcohol-acetone mixture gave white crystals (1.2 g.), m p. 234°. This product gives no coloration with alcoholic ferric chloride, chloroform-conc. sulphuric acid and acetic anhydride-conc. sulphuric acid. This product is being further investigated. The bicarbonate and hydrochloric acid extracts did not give any crystallisable product.

Swertinin.--Swertinin is soluble in alcohol, chloroform, acetone and benzene; very sparingly soluble in petroleum ether and sulphuric ether and insoluble in water and in dilute hydrochloric acid. It dissolves in sodium hydroxide to give a deep yellow solution, and in concentrated sulphuric acid to give an orange solution. With alcoholic ferric chloride it gives a green coloration. It reduces ammoniacal silver nitrate solution. [Found: C, 62.2; 62.3; H, 4.0; 4.6; OCH_3, 21.3; M. W. (Rast), 283.6; 281.1. $C_{15}H_{12}O_6$ requires C, 62.4; H, 4.2; $2OCH_3$ 21.5 per cent. M. W., 288].

The *acetyl derivative*, prepared by heating swertinin (0.2 g.) with acetic anhydride (5 c.c.) and a drop of pyridine on a steam-bath for 4 hours, was crystallised from alcohol in white needles, m.p. 157°. (Found: C, 61.3; H, 4.5. $C_{19}H_{16}O_8$ requires C, 61.3; H, 4.3 per cent). The acetyl derivative is insoluble in alkali and gives no coloration with alcoholic ferric chloride.

Methylation of Swertinin.--Swertinin (0.3 g.), dissolved in dry acetone (50 c.c.), potassium carbonate (0.7 g.) and methyl iodide (3 c.c.) were refluxed on a water-bath for 18 hours. The acetone was filtered off and evaporated. The substance obtained on removal of acetone was crystallised from alcohol in yellow needles, m.p. 150°. Mixed melting point with decussatin, obtained from the flowers, was not depressed.

When the methylation was carried out for 48 hours, out of 200 mg. of the substance, 50 mg. were fully methylated and the remaining was partially methylated. Melting point of the fully methylated compound is 165°. Mixed melting point with the fully methylated decussatin was not depressed.

Extraction with Absolute Alcohol: Attempted Isolation of the Bitter Constituent.—After extraction with ether the stems were extracted repeatedly with absolute alcohol by soaking them in alcohol (10 litres) overnight. On removal of the alcohol under reduced pressure a dark brown, resinous mass, extremely bitter in taste, was obtained. The substance remained in the solid state on keeping in a desiccator and turned into a paste on exposure to air. The resinous mass was found to be insoluble in ether, petroleum ether, benzene and carbon tetrachloride, sparingly soluble in acetone and chloroform and soluble in alcohol, methanol, ethyl acetate and water.

All attempts at purification of the material by crystallisation from different solvents, treatment with basic lead acetate, and by means of acetylation were unsuccessful. A pasty unworkable product was obtained in all cases.

The resinous bitter material was then subjected to hydrolysis with 10% alcoholic hydrochloric acid in cold in presence of coal gas for 48 hours. A dark brown precipitate was obtained on dilution of the reaction mixture with water. This mass was extracted with rectified spirit when a yellow product was obtained, which on repeated crystallisation gave yellow needles, m.p. 217°. Mixed melting point with swertinin was not depressed.

The filtrate from the above hydrolysis experiment was neutralised with sodium bicarbonate and tested for sugar. Positive tests were obtained with Benedict's and Fehling's solution, but attempts at the isolation of sugar from this solution either as such or in the form of its osazone were unsuccessful.

Extraction of Roots

Extraction with Petroleum Ether and Sulphuric Ether.—The roots which were very bitter in taste, were sun-dried and repeatedly extracted by soaking in petroleum ether (1 kg. in 6 litres petroleum ether, boiling range, 40°-60°) for 24 hours. A yellow product separated on concentration of the solvent, and crystallisation from alcohol gave deep yellow needles, m.p. 149-50°. Mixed melting point with decussatin obtained from the flowers was not depressed. The complete removal of ether gave only a greenish pasty mass.

A very small quantity of a sticky mass was obtained from the ether extract of the roots.

Extraction with Absolute Alcohol and Acetone.—The extraction was carried out as before in the cold. When the alcohol was removed under reduced pressure a brown-coloured resinous mass (approx. 50 g.), melting range 50-80°, was obtained. It was very bitter in taste. Its properties were similar to the bitter resinous mass obtained from the stems. Elaborate attempts were made for the purification of this product as in the case of the product obtained from the stems, but no definite product could be isolated. Acetone extract of the roots gave a negligible residue on removal of acetone.

Moisture Content and Inorganic Constituents of Flowers

The flowers were dried at 40° in an air-oven to a constant weight. Percentage of moisture found was 62.

The flowers were strongly heated to a constant weight. The ash obtained was 4%. This was subjected to qualitative and quantitative inorganic analysis. The following are the constituents and their percentages.

Constituent.	Percentage.	Constituent.	Percentage.
SiO_2	3.24	K_2O	14 89
Fe_2O_3	11.29	P_2O_5	3 59
Al_2O_3	6.75	Sulphate	3.70
CaO	10.12	Chloride	31.55
MgO	3.19	Carbonate	0.75
		Total.	88.06

The amount of sodium has not been determined.

Grateful thanks of the authors are due to Dr. S. A. Hakim for suggesting and supplying the plant, to Rev. Fr. Santapau, Head of the Botany Department, St. Xavier's College, Bombay, for identifying the plant, and to Prof. Jones and Dr. Halsall of Manchester University for specimens of sodium salt of oleanolic acid and the acetyl derivative of oleanolic acid.

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CHEMICAL INVESTIGATION OF INDIAN MEDICINAL PLANTS. PART II. INVESTIGATION OF *SWERTIA DECUSSATA*. STUCTURES OF DECUSSATIN AND SWERTININ

By Miss S. R. Dalal, Suresh Sethna and R. C. Shah

The two products, Decussatin and Swertinin, isolated from *Swertia decussata*, as mentioned in Part I, have been tentatively assigned the structures of 3 :4 :7-trimethoxy-8-hydroxyxanthone and 3 : 4-dimethoxy-7 : 8-dihydroxyxanthone respectively.

In Part I (this *issue*, p. 457) the isolation of two products, Decussatin and Swertinin, from the plant *Swertia decussata* and their properties have been described. Attempt is made in the present paper to arrive at their structures.

The yellow colour of decussatin indicates that it may be either a flavone or a xanthone derivative. The skeletal structure of flavone requires the molecular formula $C_{15}H_{10}O_2$. The analysis of decussatin gives the molecular formula $C_{16}H_{14}O_6$. The presence of three methoxyl and one hydroxyl groups has also been proved. This precludes the possibility of a flavone structure. The xanthone skeletal structure requires $C_{13}H_8O_2$. If we substitute one hydroxyl and three methoxyl groups, the analysis would agree with $C_{16}H_{14}O_6$. Decussatin is not at all affected by prolonged refluxing with alcoholic potassium hydroxide of various strengths varying from 10% to 40%. Xanthones are known to be stable towards alcoholic alkali, whereas the flavones usually break down under these conditions. Further, the presence of xanthones has been noted in various plants belonging to the Natural Order Gentianaceae (Shinoda, *J. Chem. Soc.*, 1927, 1983; Sashina *et al.*, *Bull., Chem. Soc. Japan*, 1942, **17**, 104; Nakaolei and Hida, *J. Pharm. Soc. Japan*, 1943, **63**, 554).

Attempts were made to arrive at the structure of decussatin by degradation. The product was subjected to the action of pulverised sodium in dry xylene for 10 hours but no definite product could be isolated from this reaction. A part of it was recovered unchanged. Attempts were made to degrade it by fusion with potassium hydroxide and sodium hydroxide mixture but no definite product could be isolated. The brown paste obtained was tested for various phenols by means of colour reactions. It gave with concentrated sulphuric acid and glycerol a reddish violet coloration, characteristic of pyrogallol, as seen by direct comparison (cf. Huntress and Mulliken, "Identification of Pure Organic Compounds : Order I", 1946, p. 236). The original compound did not not give this test.

Pyrogallol in the quantity expected in the xanthone taken for above fusion was heated under similar conditions with the alkali mixture and the reaction mixture subjected to the colour reaction. The violet colour was obtained.

The degradation of a xanthone by fusion with caustic potash is difficult and gives very low yields of the degradation products (cf. Raistrick and Robinson, *Biochem. J.*, 1936, **30**, 1303). It was not possible to repeat the fusion experiment with larger quantity as more product was not available.

As decussatin and swertinin are interrelated, the data obtained for swertinin may be discussed here.

Swertinin is deep yellow in colour and analysed for $C_{15}H_{12}O_6$. Its acetyl derivative analysed for $C_{17}H_{16}O_7$ indicating that two hydroxyl groups are methylated.

Swertinin dissolves readily in dilute alkali to give a deep yellow solution. It gives a green coloration with alcoholic ferric chloride, and an orange solution with concentrated sulphuric acid. It does not give any coloration with sodium amalgam nor pink coloration with magnesium and hydrochloric acid.

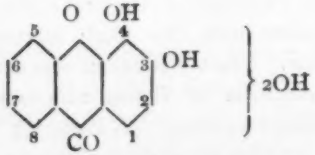
Zeisel's determination indicates the presence of two methoxyl groups. The completely demethylated product darkens at 320° and melts at 335°. It analysed for $C_{13}H_8O_6$ and its acetyl derivative analysed for $C_{21}H_{16}O_{10}$, thus indicating the presence of four hydroxyl groups in the demethylated swertinin.

The completely demethylated product from swertinin gives a green coloration with alcoholic ferric chloride which turns red on addition of sodium carbonate. The green colour is deeper in this case than in the case of swertinin. It reduces ammoniacal silver nitrate and gives a brown coloration with ammonium molybdate in molybdic acid. These reactions indicate that two hydroxyl groups are in *ortho* position to each other. The completely demethylated product does not change colour when its alkaline solution is exposed to air, thus indicating the absence of three vicinal hydroxyl groups. No reaction was obtained with *p*-benzoquinone as obtained in the case of 5: 8-dihydroxyflavone (cf. Neelkantam, Rao and Seshadri, *Proc. Ind., Acad. Sci.*, 1941, **14A**, 106), thus indicating the absence of hydroxyl groups in 1:4 and 5:8 positions.

On partial methylation of swertinin, decussatin was obtained. The mixed melting point of fully methylated swertinin and decussatin was also not depressed. Thus, swertinin contains one methoxyl group less than decussatin.

The brown paste obtained on fusion of swertinin with NaOH-KOH mixture at 240° was tested with concentrated sulphuric acid and glycerol when a red coloration was obtained, characteristic of pyrogallol, as seen by direct comparison (Huntress and Mulliken, *loc. cit.*). Swertinin did not give this test. Attempts to isolate a pure degradation product by crystallisation, acetylation etc., of the brown paste did not succeed.

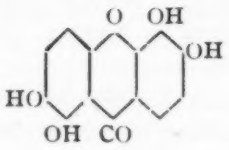
The formation of pyrogallol on fusion with alkali, and the green coloration with alcoholic ferric chloride, indicative of the presence of two hydroxyl groups in *ortho* position to each other, suggest that out of the four hydroxyl groups in all in the demethylated product, two hydroxyl groups must be situated in the xanthone skeletal structure, as shown in (I)



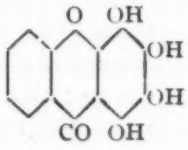
(I)

Decussatin contains three methoxyl groups and gives a brown coloration with alcoholic ferric chloride. This indicates that the free hydroxyl group must be in the vicinity of carbonyl group. Thus, the third hydroxyl group may be in position 1 or 8 in structure (I).

Swertinin contains two free hydroxyl groups which must be in the *ortho* position to each other. Swertinin on partial methylation gives decussatin which contains only one free hydroxyl group. As decussatin gives a brown coloration with alcoholic ferric chloride, this free hydroxyl group must be in the vicinity of the carbonyl group, and as swertinin contains two hydroxyl groups and gives a green coloration with alcoholic ferric chloride, the second hydroxyl group must be in the *ortho* position to the hydroxyl group in position 1 or 8. Two structures (II or III) are therefore possible for the completely demethylated product.

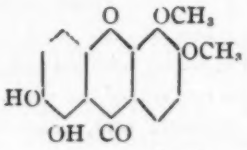


(II)

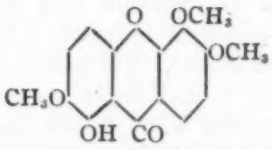


(III)

The demethylated product does not change colour in alkaline solution which indicates that three hydroxyl groups are not in vicinal positions. The completely demethylated product must therefore have structure (II) and swertinin and decussatin must have structures (IV) and (V) respectively. The fact that decussatin is difficult to methylate, further lends support to the structure assigned. Swertinin and decussatin are therefore tentatively assigned the structures 3:4-dimethoxy-7:8-dihydroxyxanthone and 3:4:7-trimethoxy-8-hydroxyxanthone respectively.



(IV)



(V)

The isolation of the xanthones in the present work is of interest as very few xanthones have so far been isolated from natural products.

EXPERIMENTAL

Action of Sodium on Decussatin in Xylene Solution.—Decussatin (0.5 g.) was dissolved in dry xylene and added to pulverised sodium (5 g.) in xylene. The mixture was refluxed on a wiregauze for 10 hours. The product obtained on working up the reaction mixture was found to be the unreacted decussatin.

Fusion of Decussatin with Alkali.—Decussatin (1 g.) was fused with sodium hydroxide-potassium hydroxide mixture (5 g.) at 240° for 2 hours and further at 300°

for half an hour. The melt was cooled and dissolved in water. It was then acidified and extracted with ether. A dark brown pasty mass was obtained. This was tested for various phenols through colour reactions. It gave reddish violet coloration with glycerol and concentrated sulphuric acid which is characteristic of pyrogallol, as seen by direct comparison.

Demethylation of Swertinin.—Swertinin (0.5 g.) was dissolved in acetic anhydride (5 c.c.) and distilled hydriodic acid (*d* 1. 7,4 c.c.) slowly added. The reaction mixture was refluxed in an oil-bath at 120° for 16 hours and then poured in a saturated solution of sodium bisulphite. The precipitate obtained was filtered and washed with hot water and crystallised from absolute alcohol-chloroform mixture. The product darkens at 320° and melts completely at 335°. It leaves no residue on heating on a spatula. It gives a green coloration with alcoholic ferric chloride which is deeper than that given by the original compound. It reduces ammoniacal silver nitrate. It dissolves in alkali to give a yellow solution which does not change colour on keeping. (Found: C, 58.8; H, 2.9. $C_{13}H_8O_6$ requires C, 59.6; H, 3.1 per cent).

The *acetyl derivative* was prepared by heating demethylated swertinin (0.2 g.) with acetic anhydride (5 c.c.) and a drop of pyridine on a steam-bath for 6 hours. The product obtained was crystallised from alcohol in colorless needles, m.p. 208°. It does not give any coloration with alcoholic ferric chloride. (Found: C, 58.3; H, 3.8. $C_{21}H_{16}O_{10}$ requires C, 58.9; H, 3.7 per cent).

Action of Alcoholic Potassium Hydroxide on Swertinin.—Swertinin (0.5 g.) was dissolved in alcoholic potassium hydroxide (20%, 10 c. c.) and refluxed on a water-bath for 8 hours. Most of the alcohol was then removed by distillation and the reaction mixture acidified with hydrochloric acid. The product obtained was crystallised from alcohol-chloroform mixture, m.p. 217°. Mixed melting point with swertinin was not depressed.

Fusion of Swertinin with Alkali.—Swertinin (1.5 g.) was fused with sodium hydroxide-potassium hydroxide mixture (7.5 g.) for 4 hours at 240° and for further half an hour at 280°. The reaction mixture was poured in water, acidified and extracted with ether. A dark brown pasty mass was obtained on removal of the ether. It gave a red coloration with glycerol and concentratend sulphuric acid, characteristic of pyrogallol, as seen by direct comparison.

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ON THE FREE SURFACE ENERGY OF SOLUTE PARTICLES AT NUCLEATION FROM SUPERSATURATED SOLUTIONS

By B. S. Srikantan and G. Venkateswarlu

The surface energy at nucleation (σ_n) of a solute has been defined as that necessary to bring the nucleus of dimension 10Å into existence in a saturated solution. This has been calculated from reliable previous data on supersolubility for sparingly soluble solutes and those where (σ_n/T) is constant. Born and Stern's surface energy of separation (σ_0) of a unit cell (dimension in Å) about planes (1 0 0) of minimum energy is found to be equal to σ_n for a number of solutes, if allowance is made for the difference in dimensions of the cell and the nucleus, and when the number of unit cells to the nucleus and the shape of the crystal are taken into account. The nucleus possesses the characteristic crystalline shape of the solute and is formed from the most favourable position of the ions of the solute arranged symmetrically to form the lattice unit. Solubility curves, which are not linear, are attributed to the polymorphic forms or structural changes which solutes are known to exhibit, as for example in the cases of $KClO_4$, KNO_3, NH_4Cl and others.

The free surface energy, σ, of solute particles has been calculated by different authors from their studies on supersaturation. The experimental conditions have been so different that more than one value has been mentioned for the same substance in literature. Thus, for gypsum σ has been given as 1050, 136 and 370 ergs/cm^2. (cf. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. I, p. 508; Hulett, *Z. Physik*, 1910, **37**, 385; Dundon, *J. Amer. Chem. Soc.*, 1923, **45**, 2665) and for barium sulphate, 520, 1250 and 3000 ergs/cm^2. (Mellor, Hulett and Dundon, *loc. cit.*). These authors have graded particles to the order of a tenth of a μ, and from the increased solubility over the normal solubility calculated σ from the Ostwald-Freundlich equation (*Z. physikal. Chem.*, 1900, **34**, 495; "Kapillarchemie", 1909, p. 44).

Ostwald-Mier's (*Z. physikal. Chem.*, 1897, **22**, 306; *J. Inst. Met.*, 1927, **37**, 331) metastable region has been shown (Srikantan, this *Journal*, 1949, **26**, 60) to be bound on normal solubility side by particles of size μ and on the labile region, by particles of size $\mu\mu$, thus arriving at the size of the nucleus for spontaneous crystallisation from supersaturated solutions to be 10^{-7} cm. Making use of this idea Venkatachallam and Srikantan (*ibid.*, 1952, **26**, 608)* have proposed a method of calculating from supersolubility data, the free surface energy of solute particles at nucleation (σ_n) from supersaturated solutions, and have calculated σ_n for a few inorganic salts. Thus, for potassium chloride under Mier's (*loc. cit.*) condition of *continuous shaking*, the value of σ at nucleation at 318Å is 3.09 ergs/cm^2. Preckshot and Brown (*Ind. Eng. Chem.*, 1952, **44**, 1314) working on *quiet* supersaturated solutions of potassium chloride report a value of 2.94 ergs/cm^2. at the same temperature. The two values agree very closely. They also show that the side length of a cubic crystal in equilibrium with its solution should be of the order of 10^{-7} cm. Hence, one obtains a more rigid definition of the free surface energy of a solute particle as that energy possessed by nuclei just to produce the aggregate as a new

* A correction has to be made in this paper. In Table I, p. 609, columns 6 and 7, the values are to be divided by 10.

phase in the presence of its saturated solution. In view of the above, it is the object of this paper to recalculate the values of σ_n for some substances (on the basis that spontaneous nucleation occurs at the particle size of 10^{-7} cm.) by the method outlined in the previous paper (*loc. cit.*) and to seek a correlation between σ_n and other properties of the solutes.

Partington and Jones (*Phil. Mag.*, 1915, **29**, 35) from theoretical considerations conclude that σ is a linear function of T, the absolute temperature. This is true most likely for sparingly soluble solutes. Venkatachallam and Srikantan (*loc.cit.*) have shown that for potassium chloride, the temperature coefficient of solubility of which is constant over the range, σ/T is constant giving a value of 0.0101 (average). But for substances like potassium nitrate and ammonium chloride, the temperature coefficient of solubility which is not constant, the linear relationship between σ and T is not obtained throughout. Dundon (*loc. cit.*) has worked on the sparingly soluble substances and found the percentage supersolubility of substances like calcium fluoride, lead iodide, strontium sulphate, barium sulphate etc., at particle sizes ranging from 0.1 to 0.5 μ. From that data the following table has been constructed for values of $r = 10^{-7}$ cm.

It has been shown previously for gypsum (Srikantan, this *Journal*, 1945, **22**, 45) that if σ/T is constant,

$$r_1\left\{\frac{S_{r_1}-S_n}{S_n}\right\} = r_2\left\{\frac{S_{r_2}-S_n}{S_n}\right\}$$

where r_1 and r_2 are the radii of the solute particles, and S_{r_1} and S_{r_2} are the corresponding values of supersolubility, and S_n, the solubility at $T°$ A and $S_r - S_n/S_n$ being the supersolubility coefficient. If $r_2 = \mu\mu$ and $S_{r_1} - S_n/S_n = \%$ increase in the solubility × solubility in moles per liter at $T°$ A, $S_{r_2} - S_n/S_n$ can be calculated.

Substituting these values in the Ostwald-Freundlich equation, one obtains σ_n at nucleation

$$\sigma_n = r_2\left\{\frac{S_{r_2}-S_n}{S_n}\right\} \times \frac{RTd}{2M} \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

where the terms have the usual significance. Values of σ_n so calculated are given in Table I, columns 3 and 6.

TABLE I

Solute.	Temp. (absolute).	σ_n (ergs/cm^2.).	Solute.	Temp. (absolute).	σ_n (ergs/cm^2.).
PbI_2	303°	0.266	$SrSO_4$	303°	1.076
PbF_2	298°	2.250	Ag_2CrO_4	299°	0.093
CaF_2	303°	0.604	$CaSO_4,2H_2O$	303°	0.230

In equation (1) σ_n is the surface energy in ergs/cm^2. for one molecular volume contained in a sphere of radius $r = 10^{-7}$ cm.

Surface Energy of Nucleation and the Surface Energy of a Unit Cell

Taking into account the electrostatic forces of attraction and repulsion between the ions in an ionic crystal, the surface energy of a unit cell has been arrived at by Born and Stern (*Sitz. Preuss. Akad. Wiss.*, 1919, 901) as

$$\sigma_c = k\frac{e^2}{a^3} \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

where k is a constant, e is the charge on an ion in electrostatic units, and a, the edge-length (distance) of a cube cell in an ionic crystal of the type AX. The value of k is 0.116 for (1 0 0) lattice plane and 0.318 for (1 1 0) lattice plane of a cubic crystal, thus showing that the minimum energy is for (1 0 0) plane along which the line of cleavage occurs if a crystal is separated. σ_c, the surface energy of a unit cell, is in ergs/cm^2.

When crystallisation is taking place from a slightly supersaturated solution, the surface energy, which brings into existence the nucleus from an ordered arrangement of ions in solution, will be just equal to the energy which disrupts the solid back into the ordered arrangement in solution as ions. This could be demonstrated if σ_n and σ_c are considered under similar conditions. Thus, it could be shown

$$\sigma_n = \frac{\sigma_c \times n}{10V} \quad \ldots \quad \ldots \quad \ldots \quad (3)$$

where V is the molecular volume of the substance, and n is the number of unit cells required to give a nucleus of crystalline shape or form.

Thus, potassium chloride, co-ordination number of which is 6 for both K^+ and Cl^- and crystallising in octahedral form, requires eight unit cells of cubic type. Further, the number 10 in the denominator is the order of increase in area per cm^2. per sphere if the change in dimension is from 10^{-8} cm. (cell) to 10^{-7} cm. (nucleus). The above calculation holds good if all the spheres are arranged with centres in a line with each other. If, however, the spheres are 'meshed' with centres of spheres of alternate layers displaced at a distance equal to the radius of a sphere, the σ_c must be further multiplied by 1.42 ($4.34/\pi$) which is the factor for the increase in area per cm^2. of sphere for this arrangement over the previous one.

The following table gives the data for σ_n and $\sigma_c \times n/10V$ for different solutes. The crystallographic data have been taken from Clark ("Fine Structure of Matter", Vol. I, Chapman and Hall, 1937); the solubility data are from the International Critical Tables. In Table II, the data for the different types of solutes are classified and presented.

TABLE II

Solute.	Crystal shape.	Unit cell.	n.	$\frac{\delta_c \times n}{10V}$	σ_n (ergs/cm^2.).		Data for δ_n (Ref.).
CaF_2	Cubic	Fluorite	1	0.668	0.604	at 303° A	Dundon
KCl	Octahedron	Cube (f c c)	8	3.27*	3.74	293°	Venkatachallam
					3.13	313	and
					3.09	318	Srikantan
					2.94	318	Preckshot & Brown.
NH_4Cl	(a) Cube Octahedron or trapezohedron feathery mass	Cube (b c c)	1	(a) 1.33	1.46	305	Venkatachallm & Srikantan
				(b) 2 048	2.04	336	
PbF_2**	(a) Ortho-rhombic	(Fluorite)	1	2.27	2.25	298°	Dundon
PbI_2	Monoclinic	Hexagonal laver lattice of CdI_2	1	0.288	0.256	303°	,,
$KClO_4$**	(a) Rhombic bipyramidal	Cubic	1	2.07	2.12	313	Venkatachallam and Srikantan
					2.02	323	
					(6.25	278)	
$CaSO_4$, $2H_2O$	Monoclinic	Cubic	1	0.293	0.230		Dundon
KNO_3	Rhomboderal to rhombic	Polymorphic		—	4.05	293°A	Venkatachallam & Srikantan
					7.15	303	
					6.33	323	
					5.81	333	

*$\frac{\sigma \times n}{10V}$ is multiplied by 1.42 (see the Discussion).

** The figure 10 in the denominator is deleted (see Discussion).

DISCUSSION

CaF_2 has a typical fluorite structure of its own. The values in columns 5 and 6 (Table II) agree. The octahedral potassium chloride crystals are f c c and require 8 units of the cube (lattice) cell and the factor $n=8$ has been introduced. Further, as the data in columns 5 and 6 agree (see footnote under Table II) it is to be presumed that the molecules are to be nested (if molecules are considered as spherical) with centres of spheres of alternate layers displaced at a distance equal to the radius of the sphere.

Ammonium chloride is a peculiar substance. Its temperature coefficient of solubility is not constant, nor does δ/T constant throughout (this *Journal*, *loc.cit.*). The structure of this substance at a high temperature (189°C) is known to be of rocksalt type and at ordinary temperatures it is of cesium chloride type (b c c). Further, the ammonium ion has not the usual tetrahedral structure, but is spherical ; the ammonium ion is known to rotate about a mean position. Again, the b c c lattice can be with the ammonium ion at the centre or chloride ion, whilst these have different intensities of reflexion for

X-rays as against potassium chloride where K^+ and Cl^- have almost equal intensity. In the cubic structure (b c c) of ammonium chloride the distance of edge cube d, where two similar ions are there, can be taken as the edge side or $\sqrt{3}/2$ times d where the distance between two unlike contiguous ions along cube diagonals is taken. For ammonium chloride d is either 3.86Å or 3.34Å. For σ_a different values are obtained at different temperatures (this *Journal, loc. cit.*) ranging between 1.46 and 2.18, and in Table II the corresponding values are quoted (*a*) for side 3.86Å and (*b*) for 3.34Å.

β-Lead fluoride is somewhat of the fluorite structure (above 200°C) with side edge 5.93Å. At lower temperatures it cryrstallises in ortho-rhombic form (α-PbF_2). Since there is no face-centered cube in the unit, the value of a^3 (or volume) in equation (2) for α-PbF_2 can be taken as the value of an equivalent body-centred cell with a square base whose edges are $1/\sqrt{2}$ times that of the original (cf. Bunn, "Chemical Crystallography", p. 222, Oxford University Press, 1945). The total side length of this equivalent cell containing all the symmetrical planes is about the length of a nucleus in Å units. Hence, the factor 10 in the denominator of equation (3) is omitted in this case as also for similar rhombic crystals of potassium perchlorate. Supersolubility of lead fluoride is one of the most carefully worked out solute by Dundon.

Lead iodide crystallising in monoclinic shape is built of hexagonal layer lattice of the type of cadmium iodide. The volume factor for equation (2) is obtained from the formula (Birge, *Rev. Mod. Phys.*, 1941, **13**, 133)

$$M = V \text{ (in Å}^3) \times 10^{-24} \times d/1.6604 \times 10^{-24}.$$

Gypsum crystallises in monoclinic form and the above formula (Birge, *loc. cit.*) for volume is utilised.

Potassium perchlorate is known to crystallise in two forms, α and β. α is the rhombic bipyramidal form usual at ordinary temperature; however, tabular crystals have been obtained by spontaneous crystallisation of cold saturated solutions (Mitscherlich, *Pogg. Ann.*, 1832, **25**, 300). The size of the side of the unit cells (α-form) are about that of the nucleus in Å units and 10 is omitted in the denominator of equation (3). However, at 278°A the value of σ_n is 6.25. The volume factor for equation (2) is taken as 2 (abc × 1/3) where a, b and c are the three sides, *i. e.*, the shorter axes of the rhomb, ending at the corners. The solubility curve is not a straight line.

The solubility curve of potassium nitrate suddenly rises up showing high increase in solubility with temperature after about 25°. The value of σ_n also suddenly changes to a high value between 20° and 30° and falls gradually with temperature. This substance is well known for its exhibition of polymorphism. Mellor (*loc. cit.*, Vol. II, p. 809) mentions that from a slightly supersaturated solution rhombohedral crystal plates, which are first formed, are followed by needle shaped rhombic crystals. It exhibits dimorphism at 129°. Bridgman (*Proc. Amer. Acad.*, 1916, **51**, 579) while studying the polymorphism of potassium nitrate has shown that at 21.3° a triple point occurs showing the existence of forms II, III, and IV. Further, the nitrate ion is known to rotate.

The data in columns 5 and 6 in Table II agree fairly well for a number of ionic crystals. It is evident from the foregoing that supersaturated solutions of inorganic salts (ionic crystals) present the most favourable arrangement of ions in a symmetrical manner for the formation of the nuclei of the solute characteristic of the shape into which they finally grow as crystals. The surface energy of formation of nuclei is equal to the minimum surface energy of separation of the crystal nuclei into its component ions forming its lattice units. Nature of solutes whose solubility curves are not straight but show a change in temperature coefficient of solubility can be attributed to the polymorphic forms in which the nucleus can exist as in the case of potassium nitrate, potassium perchlorate or to structural differences as in the case of ammonium chloride, showing different surface energies.

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AZULENES AND RELATED SUBSTANCES. PART 1. PICRAMIDE FOR THE CHARACTERISATION AND PURIFICATION OF *s*-GUAIAZULENE*

By K. B. Dutt, Sukh Dev and P. C. Guha

Picramide forms a stable molecular compound with *s*-guaiazulene. Three techniques have been described for the regeneration of the azulene. A picryl chloride complex is also described.

Sherndal (*J. Amer. Chem. Soc.*, 1915, **37**, 1537) and Ruzicka and Rudolph (*Helv. Chim. Acta*, 1926, **9**, 118, 132) recommended the use of picrates and styphnates for the isolation and characterisation of azulenes. The picrates and styphnates are usually well crystalline substances, from which the parent azulene can be easily regenerated in the pure form by treatment with liquor ammonia. Pfau and Plattner (*ibid.*, 1936, **19**, 858) found that, in general, the picrates and styphnates were stable only in the presence of excess of reagents, and pointed out the superiority of trinitrobenzene ("trinitrobenzolate") and trinitrotoluene ("trotylates") complexes. These latter double compounds have definitely superior crystallising power, and in view of their being sparingly soluble in alcohol, are always obtained in better yields. However, unlike the picrates and styphnates, the regeneration of the azulene component is not so easy. The double compounds must first be treated with a reducing agent like ammonium sulphide, which will reduce a nitro group of the polynitrohydrocarbon part of the molecular complex, the separation can then be readily effected by steam distillation. A milder method, introduced by Pfau and Plattner (*ibid.*, 1937, **20**, 230), is the chromatographic separation of the trotylates and the trinitrobenzolates, when dissolved in *cyclo*hexane and filtered through an aluminium oxide column. However, this method can be readily adopted only for small quantities of a compound, and in fact for the decomposition of small amounts of picrates, styphnates, trotylates, etc. This technique gives remarkable results.

A few more polynitro compounds have been tested (vide Experimental) for their capacity to form soluble complexes with *s*-guaiazulene in order to see if a reagent superior to T. N. B. could be found for the purification of this azulene. Of these, picramide has shown a special merit.

Picramide readily forms a double compound with *s*-guaiazulene in alcohol-acetic acid solution. The compound crystallises in black needles with a coppery red lustre and is obtained in a very good yield, in a more or less pure form from the crude azulene directly (the m.p. of 163.5° is quite sharp). The compound, when stored in a dry, brown coloured bottle, keeps very well, there being absolutely no change in the melting point after 2 years. For the regeneration of pure *s*-guaiazulene from the picramide complex, three techniques have been developed. It has been observed that a

*An advance communication appeared in *Science & Culture*, 1950, **15**, 488

solution of the compound in dry benzene is green in colour and the compound exists in a dissociated state. If to such a solution another miscible solvent, in which azulene should be soluble and picramide insoluble, be added, the picramide is precipitated out liberating the azulene and a pure blue-coloured solution results from which the azulene can be obtained. This method, as described in the experimental, is very suitable for the purification of small amounts of the azulene. The second technique also makes use of the dissociation of the compound in presence of *cyclo*-hexane. The method is remarkably suitable for the decomposition of comparatively large amounts of the picramide compound. The third method takes advantage of the easy decomposition of picramide on heating with aqueous alcoholic caustic soda. A benzene solution of the compound is refluxed with 10% aqueous alcoholic caustic soda till no more ammonia is evolved. A non-miscible layer of benzene is employed in order to protect the azulene from unnecessary action of the alkali. The method is suitable for the decomposition of both small and large amounts of the compound.

Picryl chloride readily forms a double complex with *s*-guaiazulene and the compound crystallises well. The azulene can be separated from this compound by treatment with alkali as described for the picramide compound.

All these methods have been described for *s*-guaiazulene, since no other azulene was readily accessible. But it is hoped that this reagent may also prove to be equally useful for other azulenes.

EXPERIMENTAL*

Preparation of s-*Guaiazulene.*—The essential oil from the wood of *Lansium anna-malyanum* (Rao, Dutt, Sukh Dev and Guha, this *Journal*, 1952, **29**, 604, 620) was used as the source of *s*-guaiazulene.

The oil (245 g.) and finely powdered sulphur (95 g., 80% of theory) were placed in a 750 c.c. modified Claisen's flask. The side-arm of the flask was connected through a safety bottle to a long wide glass tube of the size of a combustion tube filled with caustic soda flakes, which in turn was connected to a water-pump. The reaction mixture was heated in an oil-bath at 180°-190° and such a vacuum was applied that the oil refluxed but did not distil. Vigorous evolution of hydrogen sulphide took place as was indicated by the tube containing caustic soda. After 2 hours, the temperature was raised to 200°-210° and the vacuum was slightly decreased to avoid distillation of the product. The temperature was maintained at this point for one hour. The reaction mixture was then distilled off in vacuum and the distillate redistilled over some zinc dust, or better freshly precipitated copper, when it was obtained as a deep blue oil, yield 137 g.

The distillate was taken up in petroleum ether (b. p. 40°-60°, 500 c.c.) and vigorously shaken with 50, 25 and 10 c.c. portions of syrupy phosphoric acid (*d* 1.74), when the petroleum ether layer became practically colorless. The combined phosphoric acid extracts were washed twice with petroleum ether, diluted with ice-cold water and extracted with ether (twice with 150 c.c. portions). The deep blue ether

* All m.p.'s are uncorrected.

solution was dried (Na_2SO_4) and the solvent distilled off, leaving the *s*-guaiazulene as a viscous, dark coloured oil (pure cobalt blue, when viewed in thin layers) with a peculiar odour.

Preliminary Testing of various Polynitro Compounds for their Capacity to form Molecular Complexes with s-*Guaiazulene.*—A 20% alcoholic solution of the azulene was prepared. A drop or two of this solution was placed on a microscope slide, and one drop of the compound to be tested was added. The slide was then examined under the microscope. The crystals of a new compound formed could be very easily recognised, especially by its dark colour, even in the presence of an excess of the reagent. Amongst the compounds tested in this way were 2: 4-dinitrotoluene, 2 : 4-dinitrophenylhydrazine, picryl chloride, picramide, picranilide, 2 : 4: 6-trinitrobenzoic acid, 2 : 4 : 2′: 4′-tetranitrodiphenyl and 2:4:6:2′:4′:6′-hexanitrodiphenyl, 2:4:6-trinitrophenylhydrazine and 2:4:6-trinitrophenylethyl ether.

Only picryl chloride and picramide gave readily well crystalline compounds.

Preparation of Picramide Double Compound.—Picramide (23.0 g.) was dissolved in glacial acetic acid (322 c.c.) by heating. To the clear solution, thus obtained, azulene (crude, 20 g.), dissolved in alcohol (200 c.c.), was added. The compound formation took place immediately and from the dark coloured solution crystals started separating. After standing at room temperature for sometime, the crystals were filtered off, washed with two 15 c.c. portions of alcohol and dried. The product was obtained as black needles with a coppery red hue (if very thin crystals were obtained by allowing a drop of an alcoholic solution to evaporate on a slide and viewed under a microscope, some crystals of coppery red colour could be seen) ; m.p. 163-163.5° , yield 28 g. (66.5%). It was once recrystallised from alcohol containing some acetic acid, m.p. 163.5°. (Found : N, 13.2. $C_{21}H_{22}O_6N_4$ requires N, 13.1 per cent).

Preparation of Picryl Chloride Double Compound.—Picryl chloride (1.25 g.), dissolved in alcohol (5 c.c.), was mixed with pure azulene (1 g.). On cooling, black crystals with coppery hue were obtained, m.p. 97-98°, yield 2.0 g. (88.8%). (Found : N, 9.5. $C_{21}H_{20}O_6N_3Cl$ requires N, 9.4 per cent).

*Regeneration of Azulene from the Picramide-*s-*Guaiazulene Complex*

(*a*). *Separation by the Solvent Method.*—Picramide compound (1.0 g.) was covered with 2 c.c. of dry benzene and the mixture heated to refluxing. *cyclo*Hexane (30 c.c.) was introduced in 10 c.c. portions, followed by refluxing. Refluxing was continued till there were no more black particles of the picramide-azulene complex visible (about 15 min.). The mixture was cooled and diluted with 40 c.c. of petroleum ether (40°-60°). It was well cooled in ice for a few minutes and the precipitated picramide removed by filtration. The resulting deep blue filtrate was either distilled to remove the solvent and the residue distilled in vacuum to get pure azulene or it was passed through a column of alumina to remove the last trace of picramide, and the solvents removed to get the pure azulene. Yield of redistilled azulene was 0.38 g. (81%).

(*b*). *Separation by Soxhlet Extraction.*—Azulene-picramide (10 g.) was mixed with aluminium oxide (10 g.). The mixture was placed in a thimble and extracted

with *cyclo*hexane (75 c.c.) in a Soxhlet apparatus till no more azulene could be extracted, as shown by the colour of the extract. The solvent was removed under slight suction and the residue (4.3 g.) distilled in vacuum. Pure *s*-guaiazulene was obtained as dark, viscous oil, b.p. 164°-165°/9 mm., yield 3.9 g. (84%).

(*c*). *Decomposition by Alkali Treatment.*—Azulene-picramide (1.0 g.) was dissolved in benzene (20 c.c.) and an aqueous alcoholic solution of caustic soda (10%, 10 c.c.) was added. The mixture was refluxed for one hour. The benzene layer was separated and washed with water till the washings were colorless. The benzene solution was then dried and the solvent removed and the azulene distilled, yield 0.4 g. (86%).

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CHEMICAL INVESTIGATION OF THE FATTY OIL FROM THE SEEDS OF *MORINGA PTERIGOSPERMA*

By B. C. Subba Rao, K. Narayana Rao and H. Subba Jois

The seeds of *Moringa pterigosperma* on extraction with petroleum ether yielded a fatty oil (31.5%) which was found to contain the glycerides of palmitic (9.3%), stearic (7.4%), behenic (8.6%) and oleic 65.7%) acids.

The unsaponifiable matter from alcohol was obtained in a crystalline condition (m.p. 134°) which gave all the colour reactions of phytosterols.

Moringa pterigosperma (family Moringacea), commonly known as Drumstrick tree and abundant throughout India, is often cultivated in Burma, Egypt, Arabia and America. It is known by the following names in different Indian languages—Murungi or Dwishigru (Sanskrit), Shaninjan (Hindi), Murungai (Tamil), Munuga (Telegu) and Nugge (Kannada). It is a fast growing tree yielding sticks twice a year. The seeds are orange shaped, about 1 cm. in diameter. It consists of outer husk and inner kernel, rich in oil. The seeds used for this investigation were obtained from the local market of Bangalore and Mysore cities.

The leaves and pods of the tree have been worked up for their vitamin-C content, bark of the tree for alkaloid content, and ascorbic oxidase from the stick juice. The oil from the seeds is said to have a curative effect on skin diseases like leucoderma (Nadkrni, "Indian Materia Medica", p. 563). The oil is considered to be a very good lubricant for fine machinery and a highly reputed base for quality perfumes (Chopra, "Indigenous Drugs of India", 1933, p. 346).

The seeds (kernel) were successively extracted with different solvents.

Table I

	Solvents.	Extract.		Solvents.	Extract.
1.	Petroleum ether (b.p. 50°-60°)	31.5%	4.	Ethyl acetate	2.3%
2.	Ethyl ether	1.6	5.	Ethyl alcohol	12.9
3.	Chloroform	0.6		Total extractable material	48.9

The petroleum ether extract gave a pale yellow fatty oil (31.5%), containing no nitrogen or sulphur, while all other extracts (No. 2-5) consisted of brown viscous materials. The free fatty acids obtained from the oil were separated into solid and liquid acids by Twitchell's lead salt method.

The methyl esters of the solid acids were fractionally distilled under reduced pressure and the different fractions were hydrolysed, examined for individual acids and found to contain palmitic, stearic and behenic acids.

The methyl esters of the liquid acids were similarly distilled under reduced pressure and found to contain only oleic acid.

From these results the fatty acids of the oil were found to have the following composition: palmitic acid, 9.3%; stearic acid, 7.4%; behenic acid, 8.6% and oleic acid, 65.7%.

The unsaponifiable matter yielded a crystalline substance of m.p. 134°, which gave the colour reactions of phytosterols.

The husk of the seeds of *Moringa pterigosperma* on extraction with petroleum ether yielded a fatty oil (8.3%).

The glyceride composition of the fatty oil was determined by following the oxidation method of Hilditch (*J. Chem. Soc.*, 1927, 3106) as modified by Menon and Kartha (*Proc. Ind. Acad. Sci.*, 1943, **17A**, 114; 1945, **21A**, 222). The results gave the following glyceride composition for the oil: trisaturated glycerides (GS_3), 1.40%; disaturated mono-unsaturated glycerides (GS_2U), 23.47%; monosaturated di-unsaturated glycerides (GSU_2), 25.62%; tri-unsaturated glycerides (GU_3), 49.51% and the maximum proportions of the individual glycerides: palmito-diolein, 9.23%, stearo-diolein, 8.32%; beheno-diolein 8.08%; dipalmito-olein, 8.45%; distearo-olein, 7.63%; dibeheno-olein, 7.40%.

EXPERIMENTAL

The oil obtained by extraction with petroleum ether of the seeds (kernel) had the following constants.

TABLE II

1. Sp. gr. at 30°	0.8984	5. Reichert-Meisel value	0.44
2. Ref. index at 30°	1.46524	6. Acid value	3.48
3. Spon. value	182.20	7. Acetyl value	11.50
4. Iodine value	64 20	8. Hehner value	91.59
		9. Unsaponifiable matter	3.05%

Mixed Fatty Acids.—The oil (500 g.) was saponified with alcoholic potash and the resulting soap dried and extracted with ether to remove the unsaponifiable matter. The soap was then dissolved in water and acidified with dilute sulphuric acid. The liberated acids were extracted with ether and worked up as usual. The mixed fatty acids, thus obtained, had M. W., 282.75; I. V., 67.4.

Separation of Solid and Liquid Acids.—The mixed fatty acids were separated into solid and liquid acids by Twitchells lead salt method and the acids were worked up as usual: solid acids (26.85%), liquid acids (72.2%), colouring matter and resin acids (1%). They had the following constants.

TABLE III

	Mean M. W.	I. V.
Solid acids (155 g.)	289 3	3.5
Liquid acids (350 g.)	280.3	84.3

Identification of Solid Acids.—The solid acids were converted into methyl esters by Fischer-Speirs method and the methyl esters were fractionally distilled at 0.5 mm. pressure (Table IV).

TABLE IV

Fraction.	B.P.	Amount.	Mean M. W.	
1	140-154°	13.23 g.	149.4	A
2	154-156°	17.00	261 5	
3	156-159°	18.63	266.5	
4	159-162°	13.58	274 4	B
5	162-165°	12.35	275.5	
6	165-172°	7.68	292.2	C
7	172-185°	5.25	298.6	
8	Residue (highly coloured)	20.0	325.1	

Fractions A, B, and C were refractionated with results as shown in Table V.

TABLE V

	B.P.	Amount.	Mean M.W.
	Fraction A (45 g)		
A_1	140-154°	21.00 g.	261.4
A_2	154-157°	9.27	265.0
A_3	157-160°	6.73	282.0
	Residue of A + fraction B (32 g.).		
B_1	157-160°	3.20	266.8
B_2	160-165°	27.25	279.2
B_3	165-168°	5.90	287.6
	Residue of B + fraction C (12.5 g.).		
C_1	168-174°	3.72	288.8
C_2	Residue	8.30	343.8

Fractions A_1, A_2 and B_1 were mixed and hydrolysed by alcoholic potash and the liberated acid after crystallisation yielded an acid of m..p. 60.5°−61°, M. W. 255.5 and gave a *p*-phenylphenacyl ester of m.p. 93-94° ; on admixture the acid did not depress the m.p. of an authentic sample of palmitic acid.

Fractions A_3, B_2, B_3 and C_1 were mixed and hydrolysed by alcoholic potash and the liberated acid after crystallisation yielded an acid of m.p. 68-69°, M. W. 284.7 and gave a *p*-phenylphenacyl ester ; m.p. 95-96° (mixed m.p. with an authentic sample of stearic acid, m.p. 95-96°).

The remaining fraction C_2 was mixed with the residue and hydrolysed ; the liberated acid after crystallisation gave an acid of m.p. 78-79°, M. W. 342.7 and gave a *p*-phenylphenacyl ester ; m.p. 100-101°, on admixture it did not depress the m.p. of an authentic sample of behenic acid.

The composition of the solid acids was as follows: palmitic, 37.0% ; stearic, 29.0% and behenic, 33.5%.

Identification of Liquid Acids.—The liquid acids were examined by the bromine addition method of Eibner and Muggenthaler (Lewkowitsch, "Chemical Techonology and Analysis of Oils and Fats", Vol. I, 6th Ed., p.585). The liquid acids (5 g.) were dissolved in dry ether (50 c.c.) and cooled to $-5°$. Dry bromine was added dropwise till the colour remained yellow, and kept at $-5°$ for two hours. No hexabromide or tetrabromide separated.

The composition of the several acids in the oil was therefore palmitic acid (9.3%), oleic acid (65.7%), stearic acid (7.4%) and behenic acid (8.6%).

The *unsaponifiable matter*, obtained above after three crystallisations from alcohol, gave a white crystalline substance, m. p. 133-34°. It gave the colour reactions of phytosterols. The acetyl derivative of m.p. 126-27° is in agreement with that of sitosterol acetate. No definite compound could be isolated from the resin acid and the colouring matter (P_3).

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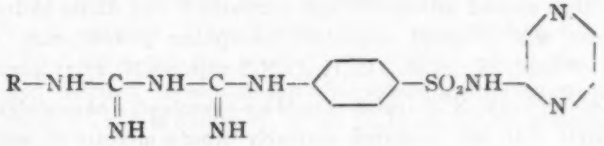
STUDIES IN ANTIMALARIALS. PART XIX. SULPHAPYRAZINE SUBSTITUTED ARYL BIGUANIDES

By P. R. Gupta and P. C. Guha

Amongst all the sulphadiazines, sulphapyrazine, (the 1 :4 analogue), has been found to be the most potent as a "suppressive cure" against malaria. In view of the importance of the biguanides in the chemotherapy of malaria, compounds having the active moieties of both these classes were synthesised and tested against experimental malaria. Activity in some of the compounds compared favourably well with that of Paludrine.

Of all the N^1-substituted sulphanilamides, tested against experimental and human malaria, sulphadiazines have shown the most promising results. Like paludrine, a few members of this series act on the exoerythrocytic forms of avian malaria (Coggeshall *et al.*, *Proc. Soc. Expt. Biol. Med.*, 1944, **57**, 286). Sulphapyrazine, the 1:4 analogue, has been found to be the most potent amongst all the sulphas as a "suppressive cure" (Findlay, *Trop. Med. Parasitol.*, 1949, **43**, 1). It is found to be the least toxic, but its lack of solubility is a great handicap.

Considering the immense possibilities of the biguanides in the chemotherapy of malaria, we were prompted to synthesise compounds having the active sulphapyrazine attached to the end-nitrogen atom of the biguanide system. This combination would help the molecule in its absorption in the system and also would help the compound to exist in various tautomeric forms, and as such will have a great influence on the antimalarial activity of the compound. Compounds of the following type have been synthesised and screened against *P. gallinaceum* in young chicks.



[where R = aryl groups, substituted or otherwise.]

Compounds having the active biguanidyl linkage attached to the N^1-atom of the sulphonamido group,

$$NH_2—C_6H_4—SO_2—NH—C(:NH)NH—C(.NH)—NHR$$

have also been reported to be useful therapeutic agents (Funke *et al.*, *Bull. soc. chim.*, 1947, 1062; B.P., 550, 538; U.S.P., 2, 295, 884).

For the preparation of the above type of compounds, sulphapyrazine was reacted with the required cyanoguanidines in dry pyridine medium having enough pyridine

hydrochloride to allow the biguanide formed to yield biguanide hydrochloride. The products were isolated, purified and characterised either as free bases or their hydrochlorides. Dioxan or any alcohol was found to be unsuitable for this condensation. The products are colorless, amorphous or crystalline substances.

Some of the above compounds (specially when R=*p*-CH_3O—C_6H_4—,) have shown high suppressive activity, which compares very well with that of paludrine. In other cases, however, the introduction of the biguanidyl linkage produced distinct dystherapeutic effect, which might be due to the complete upsetting of the chemico-physiological balances of the compounds. Curd *et al.* (*Nature*, 1946, **158**, 707) postulated that in a biguanide structure, the hydrogen bonding between N^2- and N^4-nitrogen atoms would enable the molecule to form metallic complexes and render the compounds active. In the authors' opinion, the activity of the compounds is decided by the nature of the substituents at either end which would balance the compounds chemico-physiologically and also their metabolites in the system. Under the circumstances it was considered to be of interest to study the capacity of these sulpha-biguanides towards chelation, and accord ingly attempts were made to prepare their chelates. These biguanides, however, showed very little tendency to form complexes. It was also for this reason that the copper-complex method could not be employed with success for their isolation.

For the purpose of screening the new compounds, 7-day old laboratory bred chicks were infected with parasitised cells drawn from heavily infected birds. Drugs were administered orally.

EXPERIMENTAL

N^1-*Phenyl*-N^5-p-(*sulphonamido-2-pyrazinyl*)-*phenylbiguanide* (type I, R = phenyl) (I).—A mixture of sulphapyrazine (5 g.), phenylcyanoguanidine (3.2 g.), pyridine hydrochloride (2 g.) and pyridine (15 c.c.) was refluxed for 4 hours. As no solid separated out on cooling the clear reaction mixture, it was diluted with water when a colorless solid separated out. This was then boiled with alcohol for 15 minutes, filtered hot and washed well with alcohol. The solid was then dissolved in dilute caustic soda solution which was then treated with norite and neutralised with dilute hydrochloric acid. The biguanide base was obtained as a white, amorphous powder, m.p. 238-40° (decomp.), yield 3.5 g. (Found: N, 26.98. $C_{18}H_{18}O_2N_8S$ requires N, 27.31 per cent).

N^1-p-*Chlorophenyl*-N^5-p-(*sulphonamido-2-pyrazinyl*) - *phenylbiguanide* (type I,R= *p*-chlorophenyl) (II) was prepared similarly from a mixture of sulphapyrazine (5 g.), *p*-chlorophenylcyanoguanidine (3.8 g.), pyridine hydrochloride (2.5 g.) and pyridine (20 c.c.), the mixture being refluxed for 6 hours. After the reaction was over, the clear reaction mixture was treated with dry acetone and alcohol, when a colorless solid was obtained. This was collected and washed well with hot alcohol. The biguanide base was isolated by dissolving the above solid in dilute caustic soda solution and neutralising it with dilute hydrochloric acid. It was crystallised from alcohol, m.p. 250° (decomp.), yield 4.5 g. (Found: N, 25.56. $C_{18}H_{17}O_2N_8ClS$ requires N, 25.19 per cent).

The *hydrochloride* of the above base (II) was prepared by adding concentrated hydrochloric acid to a boiling suspension of the base in alcohol. The clear solution on

cooling gave a colorless solid of the hydrochloride which was crystallised from dilute alcohol, m.p. 245°. (Found : N, 23.62. $C_{18}H_{17}O_2N_8ClS$, HCl requires N, 23.28 per cent).

N^1-p-*Bromophenyl*-N^5-p-(*sulphonamido-2-pyrazinyl*) - *phenylbiguanide* (type I, R= *p*-bromophenyl) (III), was prepared from sulphapyrazine (5 g.), *p*-bromophenylcyanoguanidine (4.5 g.), pyridine hydrochloride (3 g.) and pyridine (20 c.c.). The method followed was similar to that as described under (II). The biguanide base had an m.p. of 238°, yield 5 g. (Found: N, 22.65. $C_{18}H_{17}O_2N_8BrS$ requires N, 22.90 per cent).

The *hydrochloride* was prepared from the base (III), following the method as described in the previous case. It was crystallised from alcohol, m.p. 225°. (Found: N, 21.58. $C_{18}H_{17}O_2N_8BrS$, HCl requires N, 21.31 per cent).

N^1-p-*Anisyl*-N^5-p-(*sulphonamido-2-pyrazinyl*)-*phenylbiguanide* (type I, R=*p*-anisyl) (IV) was prepared similarly from a mixture of sulphapyrazine (5 g.), *p*-anisylcyanoguanidine (3.8 g.), pyridine hydrochloride (3 g.) and pyridine (20 c.c.), the mixture being refluxed for 7 hours. After subsequent treatment, the base was purified through its sodium salt, m.p. 245-46° (decomp.), yield 3.5 g (Found: N, 25.32. $C_{19}H_{20}O_3N_8S$ requires N, 25.45 per cent).

Hydrochloride of the base (IV) was prepared as in the previous cases and was crystallised from alcohol-hydrochloric acid mixture, m.p. 208-10° (decomp.). (Found: N, 23.81. $C_{19}H_{20}O_3N_8S$,HCl requires N, 23.50 per cent).

N^1-p-*Tolyl*-N^5-p-(*sulphonamido-2-pyrazinyl*)-*phenylbiguanide* (type I, R=*p*-tolyl) (V) was similarly prepared from sulphapyrazine (5 g.), *p*-tolylcyanoguanidine (3.4 g.), pyridine hydrochloride (3 g.) and pyridine (25 c.c.). After refluxing for 5 hours, the base was worked up and purified through its sodium salt, m.p. 241° (decomp.), yield 4 g. (Found: N, 26.72. $C_{19}H_{20}O_2N_8S$ requires N, 26.41 per cent).

The *hydrochloride* was prepared from the base (V) as described above and was crystallised from dilute alcohol, m.p. 247°. (Found: N, 24.6. $C_{19}H_{20}O_2N_8S$, HCl requires N, 24.31 per cent).

N^1-m - *Chorophenyl* - N^5-p-(*sulphonamido-2-pyrazinyl*) - *phenylbiguanide* (type I, R=*m*-chlorophenyl) (VI) was prepared from sulphapyrazine (5 g.), *m*-chlorophenylcyanoguanidine (3.8 g.), pyridine hydrochloride (3 g.) and pyridine (20 c.c.). The mixture was refluxed for 6 hours and the product was worked up in the usual way. The base was purified through its sodium salt after subsequent treatment with boiling alcohol, m.p. 248°, yield, 3.9 g. (Found : N, 25.31. $C_{18}H_{17}O_2N_8ClS$ requires N, 25.19 per cent).

Hydrochloride of the above base (VI) was prepared following the general rule as described under (II) and was crystallised from alcohol-hydrochloric acid mixture, m.p. 239-40°. (Found: N, 23.41. $C_{18}H_{17}O_2N_8ClS$,HCl requires N, 23.28 per cent).

N^1-(2-*Pyrazinyl*)-N^4-*biguanidylphenylsulphonamide* (type I, R=H) (VII) was prepared similarly from a mixture of 2-sulphapyrazine (2.5 g.), dicyandiamide (0.8 g.), pyridine hydrochloride (1 g.) and pyridine (10 c.c.). The mixture was refluxed for 7 hours. The biguanide was purified through its sodium salt, m.p. 185-86° (decomp.), yield 1 g. (Found: N, 33.21. $C_{12}H_{14}O_2N_8S$ requires N, 33.53 per cent).

Hydrochloride of (VII) was prepared in the usual way and crystallised from dilute alcohol, m.p. 216-17° (decomp.). (Found: N, 30.64. $C_{12}N_{14}O_2N_8S,HCl$ requires N, 30.22 per cent).

N^1-p-*Xylyl*-N^5-p-(*sulphonamido-2-pyrazinyl*) - *phenylbiguanide* (type I, R = *p*-xylyl) (VIII) was prepared from a mixture of sulphapyrazine (3.7 g.), *p*-xylylcyanoguanidine (2.8 g.), pyridine hydrochloride (3 g.) and pyridine (10 c.c.), the mixture being refluxed for 6 hours. The base, after subsequent treatment with alcohol, was purified through its sodium salt, m.p. 228-30°, yield 4 g. (Found: N, 25.36. $C_{20}H_{22}O_2N_8S$ requires N, 25.50 per cent).

The *hydrochloride* was prepared from the base (VIII) and was crystallised from dilute alcohol, m.p. 249-50°. (Found: N, 23.82. $C_{20}H_{22}O_2N_8S,HCl$ requires N, 23.60 per cent).

Thanks of the authors are due to the Indian Council of Medical Research for the award of a Research Fellowship to one of them (P.R.G.) and to Messrs. Mead Johnson & Co., Evansille, for a gift of sulphapyrazine.

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QUINOLINE COMPLEXES OF COBALT AND NICKEL SULPHATES AND THEIR HEATS OF FORMATION

By G. C. Bhattacharya and P. C. Sinha

Quinoline complexes of cobalt and nickel sulphates, having respectively the formula, $CoSO_4.C_9H_7N.6H_2O$ and $NiSO_4.3C_9H_7N.4H_2O$ have been prepared. Their formulae have been established by analysis. The heats of formation of the cobalt and nickel complexes have been determined by direct thermochemical methods and found to be +3, 395 and +11, 632 calories per G. M F. respectively, showing that the nickel complexes are much more stable than that of cobalt. The retarding action of the SO_4'' ion complex formation has been discussed.

The present paper records the study of the preparation and properties of the quinoline complexes of nickel and cobalt sulphates. The heats of formation of these compounds have been measured by the thermochemical methods and the application of Hess's law. The heats of formation give a measure of the order of their stability. Chang and Yü (*Z. anorg. Chem.*, 1939, **243**. 14) prepared a quinoline complex of cobalt sulphate to which they assigned the formula $2CoSO_4.C_9H_7N$. The composition of this compound is entirely different from that obtained by us. Our complexes were prepared from aqueous solutions and contained water; the cobalt and the nickel complexes were found to possess the formulae $CoSO_4.C_9H_7N.6H_2O$ and $NiSO_4.C_9H_7N.4H_2O$ respectively. It should be mentioned that quinoline complexes of zinc and cadmium also contained water, having respectively the formulae $ZnSO_4.2C_9H_7N.8H_2O$ and $CdSO_4.2C_9H_7N.6H_2O$ (Bhattacharya and Sinha, this *Journal*, 1950 **27**, 21).

Experimental

The method of preparation was similar to that employed for the complexes of zinc and cadmium sulphates described in an earlier communication (*loc.cit.*).

The complexes obtained are crystalline and possess water of crystallisation. The crystals of quinoline complex of cobalt sulphate are pinkish brown and those of nickel sulphate, light green. The complexes of cobalt and nickel are both soluble in water with difficulty. They are partially soluble in alcohol. In acetone, the nickel compound is partially soluble, whereas the cobalt complex is insoluble. Both of them are insoluble in ether. The results of dehydration experiments were inconclusive and no definite information could be obtained whether part or whole of the water in the complex went to the formation of complex ion.

For the estimation of quinoline in the compounds, a modification of the method described by Lange (*Ber.*, 1883, **21**, 579) was followed. Blank experiments with weighed amounts of purified quinoline show that the method is accurate to about 1%, mainly due to the difficulty of obtaining a sharp end-point. Several indicators were

tried but methyl orange gave the best result. Sulphate in the compound was determined as barium sulphate in the usual way after decomposing the complex. Cobalt was determined after distilling off the quinoline by steam by electrolytic deposition from a strongly ammoniacal solution containing ammonium sulphate. Nickel in the complex was determined by precipitating with dimethylglyoxime after distilling off the quinoline with steam. The analytical results are recorded in Table I.

TABLE I

	$CoSO_4\ C_9H_7N.6H_2O$.		$NiSO_4.3C_9H_7N\ 4H_2O$.	
	Found,	Calc.	Found.	Calc.
M	14.73%	15.04%	9.44%	9.56%
Q	33.4	32.92	64.36	64.08
SO_4	24.23	24.50	15 8	15.65
H_2O	27.64	27.54	12.67	11.71

[M = Co or Ni and Q = C_9H_7N]

Dissociation pressures of quinoline complexes were too low to be measured with any degree of accuracy; moreover, the presence of water in these complexes introduced complications in evaluating the dissociation pressure. In order to get over these difficulties and uncertainties, it was decided to determine the heat of formation of the complexes by direct thermochemical measurements. The calorimeter set up for the purpose was a modified form of that employed by Patrick and Grimm (*J. Amer. Chem. Soc.*, 1921, **43**, 2144) and described fully in a previous paper (*loc. cit.*). The heat of solution of quinoline was first determined in a known volume of 2*N*-sulphuric acid solution and then the heat of solution of the complex in the same standard acid each time was measured similarly. From these data heat of formation of the complex salts was calculated by the application of Hess's law of heat summation. The results obtained are shown in Table II.

TABLE II

Average value of thermal capacity of the following = + 152 cal. per degree.

Substance.	Wt.	Temp rise.	Heat of reaction.	Mean	Heat of formation.
$CoSO_4.\ C_9H_7N.6H_2O$	1.2594 g.	+0.060	+2,956 cal.	+2,885 cal.	+3,395 cal.
	1.6248	+0.075	+2,869		
	1.4221	+0.065	+2,832		
$NiSO_4.\ 3C_9H_7N.\ 4H_2O$	1.7264	+0.130	+7,310		
	1.0181	+0.075	+7,155	+7,211	+11,632
	2.0360	+0.140	+7,160		

The value of the heat of solution of quinoline using the same volume of 2*N*-sulphuric acid was previously determined and found to be +6,280 calories per G. M. F. This value was used in the present calculations. It was found difficult to dehydrate completely cobalt and nickel sulphates, and as no data are available for heats of solution of anhydrous sulphates of cobalt and nickel, the heats of formation of the complexes from anhydrous salts could not be computed. The results recorded above relate to hydrated sulphates.

Discussion

The heats of formation show that nickel quinoline sulphate is more than three times as stable as the cobalt quinoline sulphate. The difference between the formula of the quinoline complex of cobalt sulphate described in the present paper and that of Chang and Yü (*loc cit.*) is obviously due to the fact that they started with anhydrous cobalt sulphate. Hence their complex does not contain any water, but it is extremely unstable, being readily decomposed by water. It seems that introduction of water in the molecule increases its stability.

Dehydration experiments were carried out at 120° but contradictory results were obtained, since loss of water was accompanied by loss of varying amounts of quinoline. Hence, it was not possible to obtain any information whether a part or the whole of the water present in these complexes went to the formation of the complex ions.

Chang and Yü (*loc. cit.*) put forward the view that the bivalent sulphate ion exerts a retarding influence upon the co-ordination of quinoline. This view is supported by Reisenstein (*Z. anorg. Chem.*, 1898, **18**, 253) who studied the compounds, $CdSO_4.3Py.2H_2O$, $CoSO_4.3Py.2H_2O$ and $NiSO_4.3Py.2H_2O$. The retarding effect of the sulphate ion in complex formation is also evident from the following facts

The sulphates of cobalt and nickel formed complexes with quinoline with extreme slowness, requiring 18 to 20 hours' stirring before the complex salts separated. Secondly, presence of water is necessary for the stabilisation of these complexes. Ephraim (*Ber.*, 1920, **53 B**, 548) has suggested that the presence of neutral addenda, like H_2O, stabilises the structure of the crystal by filling seams which are caused by unequal pairing of the anion and cation. It would appear that the effect the of $SO_4^{"}$ ion, which tends to oppose the formation of the complex with quinoline, is neutralised by co-ordination with water molecules.

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POTENTIOMETRIC STUDIES IN OXIDATION-REDUCTION REACTIONS. PART XIV. OXIDATION WITH ALKALINE POTASSIUM PERMANGANATE

By Balwant Singh, Apar Singh and Gurdas Singh

Alkaline potassium permanganate is used as an oxidising agent and Stamm's procedure employed in the potentiometric estimations of potassium iodide, potassium iodate, potassium cyanide, methyl alcohol, glycerine, phenol and salicylic acid. The excess of potassium permanganate solution is titrated back potentiometrically against standard sodium formate.

Holluta (*Z. physikal. Chem.*, 1922, **102**, 32, 276) has shown that in the reaction between permanganate and formate, the reduction of permanganate in alkaline solution proceeds in two stages:

$$MnO_4' + e = MnO_4'' \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (1)$$

$$MnO_4'' + 2H_2O + 2e = MnO_2 + 4OH' \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

The first of these two reactions proceeds much more rapidly than the second. This is in confirmity with the observations of Sackur and Taegener (*Z. Elektrochem.*, 1912, **18**, 718). The difference of the velocities of the two partial reactions increases with rising hydroxyl ion concentration.

According to Stamm's procedure (*Z. angew. Chem.*, 1934, **47**, 191; 1935, **48**, 710) the oxidation with alkaline permanganate solution involves only the first partial reaction, *i. e.*, the conversion of permanganate to manganate and the slow conversion of manganate to manganese dioxide is not allowed to occur. To attain the highest possible oxidation velocities, the substance to be determined is added to an excess of alkaline permanganate solution. After the oxidation is finished, the excess of permanganate is titrated back with sodium formate.

$$2\,MnO_4' + 3OH' + HCO_2' = 2\,MnO_4'' + CO_3'' + 2H_2O.$$

To prevent the formate from carrying the reduction of the manganate ion to the manganese dioxide, which would occur as soon as about 90% of the permanganate originally present had changed to manganate, a barium salt was added to the reaction mixture before beginning the addition of the formate. Barium permanganate is soluble in water, while barium mangante is insoluble. The manganate ions produced by the reduction consequently are bound by the barium ions so rapidly that they are effectively removed from any further action of the reducing agent.

Heredia (*Arch. farm. bioquim. Tucuman*, 1947, **3**, 173) found the method of Stamm suitable in the volumetric analysis of potassium iodide, potassium iodate, potassium cyanide, potassium phosphite, methyl alcohol, formaldehyde and formic acid.

In the present investigation alkaline potassium permanganate has been used as an oxidising agent and Stamm's procedure employed in the potentiometric estimations of potassium iodide, potassium iodate, potassium cyanide, methyl alcohol, glycerine, phenol and salicylic acid. These compounds react with alkaline permanganate according to the following equations:

$$8MnO_4' + 8\,OH' + I' = 8\,MnO_4'' + IO_4' + 4H_2O$$
$$2MnO_4' + 2\,OH' + IO_3' = 2\,MnO_4'' + IO_4' + H_2O$$
$$2MnO_4' + 2\,OH' + CN' = 2\,MnO_4'' + CNO' + H_2O$$
$$6MnO_4' + 8\,OH' + CH_3OH = 6\,MnO_4'' + CO_3'' + 6\,H_2O$$
$$14MnO_4' + 20OH' + C_3H_5(OH)_3 = 14MnO_4'' + 3CO_3'' + 14H_2O$$
$$28MnO_4' + 40OH' + C_6H_5OH = 28MnO_4'' + 6CO_3'' + 23H_2O$$
$$28MnO_4' + 42\,OH' + C_6H_4(OH)COOH = 28MnO_4'' + 7CO_3'' + 24H_2O$$

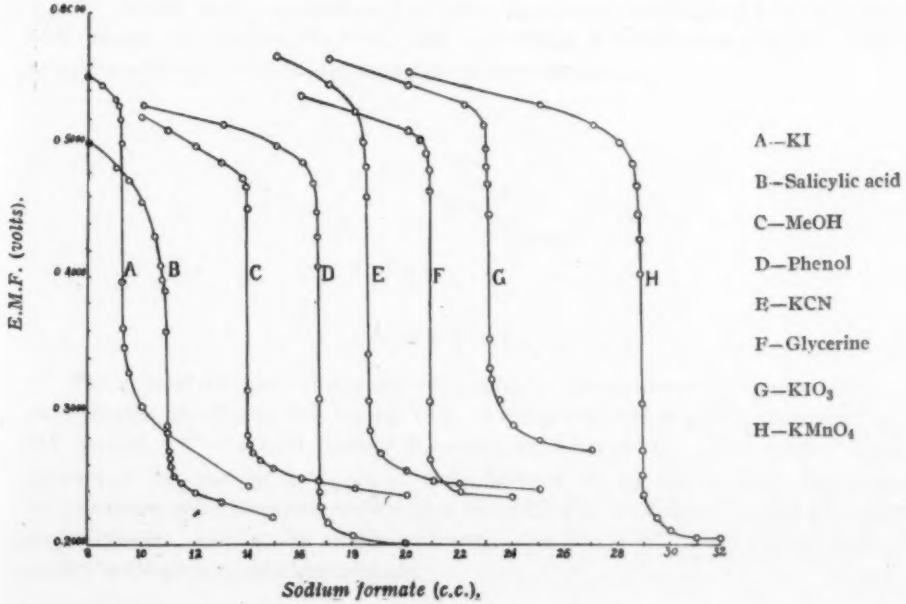
EXPERIMENTAL

A known weight of the substance was added to a known excess of standard potassium permanganate solution to which 10 to 30 c.c. of 30% NaOH solution had already been added. The mixture was allowed to stand for 10 minutes at 25°. (In case of organic compounds the mixture was warmed to 45°.) About 10 to 30 c. c. of 30% barium chloride solution was then added to the mixture and the excess of potassium permanganate solution titrated back potentiometrically against standard sodium formate solution. In these titrations the mixture was kept stirred by a mechanical stirrer.

The oxidation-reduction electrode, which consisted of a bright platinum foil immersed in a solution to be titrated, was coupled with a saturated calomel electrode through an agar agar-potassium chloride bridge. The cell was placed in a water-bath, the temperature of which was maintained at 25°. E. M. F. of the cell was read on a potentiometer.

The titrations, one for each substance, are represented by curves shown in Fig. 1.

Fig. 1



In these titrations with the addition of standard sodium formate, the E. M. F. decreased steadily till the equivalence point. At the equivalence point there was a sharp break in the E. M. F. in each case. For the addition of 0.05 c.c. of the titrant, the inflection potential was of the order of 98, 103, 94, 127, 137, 158, 92 and 71 millivolts for potassium permanganate, potassium iodide, potassium iodate, potassium cyanide, methyl alcohol, glycerine, phenol and salicylic acid respectively. After the equivalence point, there was again a fall in the E. M. F. which became steady on further addition of the reagent.

From the volume of sodium formate used, corresponding to the equivalence point in each titration, the amount of each substance was calculated.

The results show that sodium formate can be determined directly and potassium iodide, potassium iodate, potassium cyanide, methyl alcohol, glycerine, phenol and salicylic acid determined indirectly by the potentiometric method, using alkaline potassium permanganate as an oxidising agent.

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A STUDY OF THE COMPLEX FORMATION OF SALICYLAMIDE WITH URANYL ION AND A COLORIMETRIC METHOD FOR THE ESTIMATION OF URANIUM

By Amiya Kumar Chakraburtty, Debabrata Sen and Priyadaranjan Rây

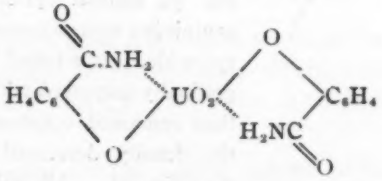
Salicylamide, which gives a yellow coloration with uranyl salts due to the formation of a complex $UO_2(C_6H_4.O.CONH_2)_2$, has been utilised for the colorimetric estimation of uranium, using Hilger-Spekker photoelectric absorptiometer. The maximum intensity of absorption occurs at p_H 6.6-7 2 in the violet region (430-440 mμ).

Sensitivity, 2γ. Influences of several foreign ions on the reaction have been given. The colour intensity has been found to obey Beer's law between 4 and 150 p.p.m. The composition and stability of the coloured complex have been determined by p_H titration following Bjerrum. $pK = 11.37$; where K is overall instability constant.

Salicylic acid and sulphosalicylic acid were found to give colour reactions with hexavalent uranium and have been conveniently employed for its detection and estimation (cf. Mueller, *Chem. Ztg.*, 1919, **43**, 739; "Analytical Chemistry of the Manhattan Project", 1950, pp. 120-21, Mc. Graw Hill).

Salicylamide, which also produces a yellow coloration with uranium^{VI}, has now been found to serve the same purpose. The maximum intensity of colour is developed at a p_H range of 6.6 to 7.2 and the maximum absorption lies in the violet region of the visible spectrum. The colour produced was found to obey Beer's law over a wide range of concentration.

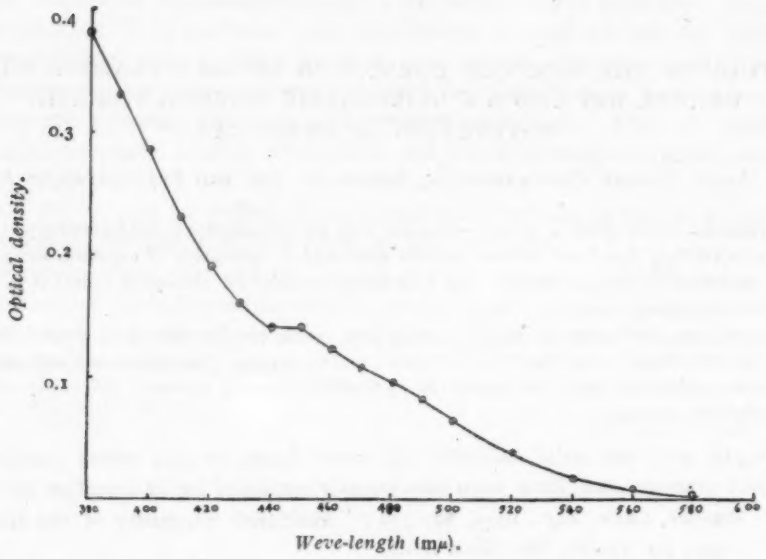
By means of p_H titration it has been found that salicylamide forms a compound with uranyl ion of formula $UO_2(C_6H_4.O.CONH_2)_2$ in two successive steps. This may be represented as a co-ordination complex of the structure :



EXPERIMENTAL

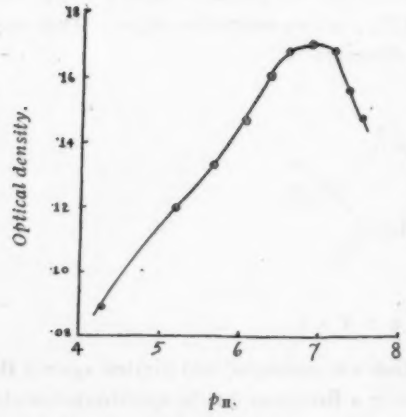
The optical density of the coloured solution was measured and plotted against the wave-lengths in the visible region (Fig. 1) using a Beckman quartz spectrophotometer (DV model). The optical density increased even beyond the visible range. There is, however, a flat portion in the O. D. curve between 430 mμ and 450 mμ. Measurements of absorption were therefore made with a violet filter in the Hilger-Spekker photoelectric absorptiometer, having the maximum transmission at 435 mμ (range 430-440 mμ). The reagent itself gives a colorless solution.

FIG. 1



Solubility and Stability of the Reagent.—The reagent is rather sparingly soluble in water. The use of solutions stronger than 0.2% is therefore not advisable. The substance, however, remains quite stable in solution.

FIG. 2



Variation of Colour Intensity with p_H.—The intensity of the colour developed varied with the p_H value of the solution. By plotting p_H against optical density for solutions containing same amounts of uranium and salicylamide, it was found that the optical density gradually increased with the p_H up to 6.6, and then remained constant till 7.2, after which the density decreased with a further rise of p_H (Fig. 2). All subsequent measurements were therefore made between 6.6 and 7.2 p_H. The colour was immediately developed and the intensity remained constant even after 48 hours.

Influence of the Reagent.—The colour was found to increase with the concentration of the reagent up to a maximum value when it remained constant. Measurements were consequently made always with a sufficient excess of the reagent permitted by its solubility. This is accounted for by the formation of the coloured complex in two successive stages as shown below while dealing with the stability of the complex formed.

Verification of Beer's Law.—A ~~0.2%~~ saturated aqueous solution of the pure recrystallised reagent was prepared. By the addition of alkali to this solution the p_H was brought near about 7.2; 40 c.c. of the reagent were added to 10 c.c. or less than 10 c.c. of the uranium solutions, neutralised as far as possible, so that the p_H of the final coloured solution might be within the prescribed region (6.6 to 7.2). The yellow colour developed immediately. The solution, nevertheless, was allowed to stand for 15 minutes before measuring its absorption in the photoelectric colorimeter. Beer's law was found to hold over a wide range of concentration (0.03 mg. to 7.5 mg. per 50 c.c.). To maintain the proper transmittancy value, measurements were made with cells of suitable sizes for solutions too weak or too strong.

Interferences by Foreign Ions at the given p_H range.—The influence of the following ions upon the colour reaction was examined and the results are given below.

TABLE I

Substance.	Ion/uranium.	Interference.	Substance.	Ion/uranium.	Interference.	Substance.	Ion/uranium.	Interference.
Na^+	1000	None	Phosphate	Very small	Precipitation	Ce^{3+}	Very small quantity	Cerium hydroxide ppt.
K^+	,,	,,	Fluoride	,,	Colour weakned	Mg^{2+}	200	None
NH_4^+	,,	,,	Oxalate	,,	Do	V (vanadate)	Very small	A greenish yellow colour was produced
Cl'	,,	,,	Citrate	,,	Do	Mo (molybdate	,,	Colour weakned
NO_3'	,,	,,	Tartrate	,,	Do	Pb^{2+}	,,	Precipitation
SO_4''	,,	,,	Th^{4+}	,,	Thorium hydroxide precipitated	Zn^{2+}	,,	Do
						Al^{3+}	,,	Do

Acetate ion, as already known, interferes due to the formation of a complex anion, as in sodium uranyl acetate, of yellow colour of much weaker intensity (cf. Ghosh and Mitter, this *Journal*, 1927, **4**, 363; Foley and Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 909).

Influence of Temperature.—The optical density of the coloured solution has been found to diminish beyond 35° as shown below.

TABLE II

Temp.	13°	25°	30°	35°	40°	45°	50°
O. D	0.140	0.138	0.139	0.138	0.130	0.128	0.125

Estimation should therefore be made at a temperature below 35°.

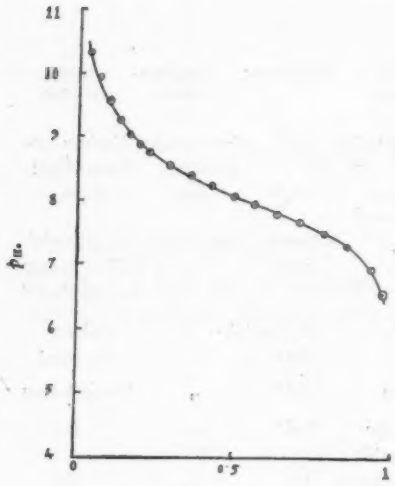
Sensitivity.—In a photoelectric filter colorimeter the minimum quantity of uranium that can be estimated is 2γ. $D = 5.7$.

Composition and Stability of the Coloured Complex.—The nature and stability of the coloured complex formed by UO_2^{++} with salicylamide was studied by physico-chemical methods following Bjerrum (cf. "Metal-Ammine Formation in Aqueous Solution", P. Haase and Son, 1941).

The experiment as usual consisted in the titration of a mixture of UO_2^{++} and salicylamide with standard carbonate-free alkali and measuring the p_H value of the mixture after each addition.

FIG. 3

Acid dissociation const. of salicylamide.

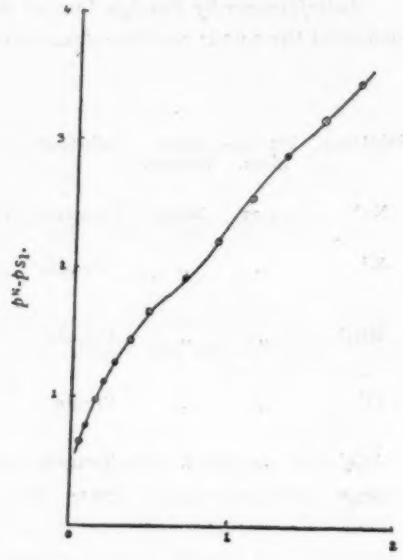


$\bar{n}$

$\bar{n}$ = Av. No. of H^+ ion bound per ligand.

FIG. 4

Titration curve of sal. amide & uranyl chloride with KOH.



$\bar{n}$

$\bar{n}_u$ = Av. No. of complex bound ligand-amide per U. atom.
S_1 = conc. of free salicylamide.

It transpired during the experiment that the reaction between UO_2^{++} and salicylamide occurs in two stages :

$$UO_2^{++} + SaH \underset{\longrightarrow}{\longleftarrow} [UO_2Sa]^+ + H^+ \quad \ldots \quad (1)$$

$$[UO_2Sa]^+ + SaH \underset{\longrightarrow}{\longleftarrow} [UO_2Sa_2] + H^+ \quad \ldots \quad (2)$$

where SaH is a molecule of salicylamide.

Therefore, the respective equilibrium constants k'_{t_1} and k'_{t_2} are :

$$k'_{t_1} = \frac{[\{UO_2Sa\}^+].[H^+]}{[UO_2^{++}].[SaH]} \quad \ldots \quad \ldots \quad (3)$$

and $$k'_{f_2} = \frac{[UO_2Sa_2] \cdot [H^+]}{[\{UO_2Sa\}^+] \cdot [SaH]} \quad \ldots \quad \ldots \quad (4)$$

and the overall equilibrium constant K'_f is given by

$$K'_f = \frac{[UO_2Sa_2] \cdot [H^+]^2}{[UO_2^{++}] \cdot [SaH]^2} \quad \ldots \quad \ldots \quad (5)$$

The acid dissociation constant, k^*, of salicylamide was determined from

$$SaH \rightleftarrows Sa^- + H^+ \quad \ldots \quad \ldots \quad (6)$$

whence $$k^* = \frac{[Sa^-] \cdot [H^+]}{[SaH]} \quad \ldots \quad \ldots \quad (7)$$

k^* was determined as usual by measuring the p_H values at intervals of a solution of salicylamide while treated gradually with an alkali solution.

From the acid dissociation constant k^* of the ligand and the p_H values, the equilibrium constants k'_{f_1}, k'_{f_2} and the overall equilibrium constant K'_f can be calculated.

The overall instability constant, K, which is equal to

$$\frac{[UO_2^{++}] \cdot [Sa^-]^2}{[UO_2Sa_2]},$$

and the instability constants of the intermediate complexes, k_1 and k_2, can then be obtained as,

$$k_1 = k^*/k'_{f_1}\ ;\ k_2 = k^*/k'_{f_2}$$

and $$K = k_1 \times k_2 = k^{*2}/k'_{f_1} \times k'_{f_2}.$$

TABLE III

Values of the various constants.

$pk^* = 8.09$ ... (cf. Fig. 3)		$pK'_f = 4.81$
$pk'_{f_1} = 1.69$	... (cf. Fig. 4)	$pk_1 = 6.40$
$pk'_{f_2} = 3.12$		$pk_2 = 4.97$
		$pK = 11.37$

From a consideration of the above values, it may be stated that the ligand salicylamide behaves as a very weak acid, and that the stability of its uranium complex approaches that of copper tetrammine ($pK = 12.6$) in aqueous solution.

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A STUDY OF THE VISCOSITY OF THE SYSTEM : WATER—SODIUM STEARATE—ALCOHOLS IN PRESENCE OF SODIUM CHLORIDE

By A. N. Bose

Viscosity of the system : water—sodium stearate—different alcohols has been studied. It has been found to behave as oleate system. Sodium stearate forms gels in presence of methyl, *iso*propyl and *n*-amyl alcohol at room temperature.

In previous communications from this laboratory (this *Journal*, 1952, **29**, 43, 135) viscosity of the soap of unsaturated acid, oleate, has been studied in presence of different alcohols. In the present paper the viscosity of the system: water-sodium stearate and different alcohols has been studied with a view to ascertaining the difference in behaviour between the soaps of saturated and unsaturated acids.

Experimental

Method of purification of chemicals and the apparatus used were the same as used in the previous work (*loc. cit.*).

Concentration of sodium strearate used was 0.2*N* instead of 0.4*N*, as used in the case of oleate. This lower concentration was taken as it was not possible to prepare a solution of 0.4*N* sodium stearate. Results obtained are shown in Table I.

Table I

Variation of viscosity with temperature and concentration.

Conc. of NaCl.	35°.	40°.	45°.	50°.	55°.
	(1) 0.2 *N* Na-stearate+30% *n*-butyl alcohol.				
Nil	0.02922	0.02556	0.02241	0.02003	0.01796
N/10	0.02966	0.02588	0.02296	0 02049	0.01835
N/20	0.02908	0.02551	0.02234	0.01995	0.01789
N/40	0.02938	0.02565	0.02252	0.01997	0.01797
	0.2 *N* Na-stearate+40% *n*-butyl alcohol.				
Nil	0.03217	0.02805	0.02445	0.02175	0.01945
N/20	0.03349	0.02917	0.02556	0.02268	0.02029
N/40	0.03248	0.02835	0.02482	0.02210	0.01967
N/80	0.03219	0.02809	0.02462	0 02194	0.01956
	0.2*N* Na-stearate+50% *n*-butyl alcohol.				
Nil	0.03388	0.02943	0.02563	0.02282	0.02025
N/40	0.03443	0.03004	0.02624	0.02328	0.02071
N/80	0.03396	0 02946	0.02568	0.02283	0.02025
	(2) 0.2 *N* Na-stearate+20% *n*-propyl alcohol.				
Nil	0.02056	0.01814	0.01601	0.01435	0.01297
N/10	0.01797	0.01591	0.01407	0.01275	
N/20	0.01891	0.01657	0.01439	0.01327	0.01209

TABLE I (contd.)

Conc. of NaCl.	35°.	40°.	45°.	50°.	55°.
		0.2 *N* Na-stearate+30% *n*-propyl alcohol.			
Nil	0.02692	0.02326	0.02026	0.01797	0.01605
N/20	0.02554	0.02231	0.01936	0.01766	0.01548
N/40	0.02594	0.02256	0.01972	0.01757	
N/80	0.02646	0.02289	0.01980	0.01767	
		0.2 *N* Na-stearate+40% *n*-propyl alcohol.			
Nil	0.02611	0.02263	0.01974	0.01747	
N/20	0.02605	0.02246	0.01960	0.01737	0.01554
N/40	0.02614	0.02261	0.01974	0.02747	
N/80	0.02611	0.02263	0.01972	0.01747	
		0.2 *N* Na-stearate+50% *n*-propyl alcohol.			
Nil	0.02629	0.02273	0.01975	0.01756	
N/20	0.02629	0.02282	0.01979	0.01760	
N/40	0.02625	0.02273	0.01972	0.01756	
N/80	0.02625	0.02271	0.01975	0.01760	

TABLE II

Variation of relative viscosity with temperature.

Conc. of NaCl.	35°.	40°.	45°.	50°.	55°.
		(1) 0.2 *N* Na-stearate+30% *n*-butyl alcohol.			
Nil	4.044	3.896	3.743	3.646	3.547
N/10	4.105	3.942	3.838	3.737	3.621
		0.2 *N* Na-stearate+40% *n*-butyl alcohol.			
Nil	4.448	4.280	4.083	3.959	3.842
N/20	4.635	4.446	4.271	4.128	4.006
		0.2 *N* Na-stearate+50% *n*-butyl alcohol.			
Nil	4.690	4.486	4.280	4.155	4.001
N/40	4.766	4.580	4.382	4.233	4.090
		(2) 0.2 *N* Na-stearate+20% *n*-propyl alcohol.			
Nil	2.845	2.766	2.673	2.611	2.557
N/20	2.617	2.525	2.403	2.413	2.386
		0.2 *N* Na-stearate+30% *n*-propyl alcohol.			
Nil	3.726	3.546	3.383	3.270	3.171
N/20	3.534	3.402	3.234	3.215	3.057
		0.2 *N* Na-stearate+40% *n*-propyl alcohol.			
Nil	3.614	3.449	3.298	3.178	3.080
N/20	3.603	3.423	3.273	3.162	3.069
		0.2 *N* Na-stearate+50% *n*-propyl alcohol.			
Nil	3.640	3.465	3.298	3.197	
N/20	3.640	3.478	3.304	3.200	

Discussion

Although the concentration of sodium stearate is 0.2*N*, but if we compare the viscosity results of Table I with the results obtained in the case of sodium oleate, it is observed that in the case of *n*-butyl alcohol the changes in viscosity are similar *i.e.*, in both the cases at 40% and 50% alcoholic concentration, the viscosity goes on increasing with the increasing concentration of sodium chloride, and in the case of 30%, the viscosity is minimum at *N*/20-NaCl concentration. Thus, it may be concluded that at 40% and 50% alcoholic concentrations, palisadal layers and the layers between the sodium ends of the stearate are saturated with the alcohol molecules. The solutions of 10% and 20% *n*-butyl alcohol could not be prepared.

In the case of *n*-propyl alcohol the behaviour of viscosity of the two systems is also the same. The concentration of sodium chloride which diminishes the viscosity at 30% and 40% is *N*/20 in both cases and in 50% alcoholic concentration, the viscosity is not diminished by the addition of sodium chloride. Therefore, at this concentration the palisadal and the layers in between the sodium ends of the stearate molecules are saturated with alcohol.

Attempt was made to prapare solutions of alcohols other than *n*-butyl and *n*-propyl, but a white gel was formed in other alcohols at room temperature. These gels transformed into sol when heated and the temperature of transition was different in the case of different alcohols. For methyl alcohol it was between 70° and 80°, in amyl alcohol, 40° and 50°, in *iso*propyl alcohol, 35° and 45°, and so the viscosity of these solutions could not be studied between the temperature range studied here.

Gels were obtained in the case of *n*-butyl and *n*-propyl alcohols when they were cooled to 5° and these gels transformed into sol at near about 15°.

It may be pointed out that the sol-gel transformation temperature was 15° in the case of *n*-propyl alcohol but it was near about 45° in the case of *iso*propyl alcohol, although the number of carbon atoms is same in both the cases.

No gel was formed for oleate solutions-even after cooling to 5°. This difference in behaviour may be due to the fact that stearic acid is saturated and the oleic acid is unsaturated.

It is suggested that in the case of sodium stearate gels are formed because a number of micelles combine together to form a big micelle and the resultant micelle is so large that it takes the form of gel and the temperature at which this gel is formed is different for different alcohols due to the difference in the streangth of the binding forces between the smaller micelles.

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CHEMISTRY OF ALIPHATIC THIOCARBAMIDES. PART I. METHYLTHIOCARBAMIDE

By R. H. Sahasrabudhey and Ranbir Singh

Chemistry of methylthiocarbamide has been investigated with respect to its formation and interaction with acids, alkalies, nitrous acid, silver nitrate, lead acetate, iodine, acetic anhydride and benzyl chloride etc. Its titrimetric estimations by iodine and mercuric nitrate are described.

Investigations of Krall *et al.* on phenylthiocarbamides (this *Journal*, 1935 onwards, Parts I to XVII) and some recent work on the oxidation products of aliphatic derivatives (Sahasrabudhey, *ibid.*, 1950, **27**, 524; 1951, **28**, 119, 309, 341) indicate marked differences in the behaviour of these two groups of compounds on oxidation. A detailed examination of the general chemistry of aliphatic substituted thiocarbamides therefore appears not without interest. This communication deals with N-methylthiocarbamide.

Formation.—Of all the methods for the formation of methylthiocarbamide described in literature (Hofmann, *Proc. Roy. Soc.*, 1874, **17**, 72 ; Andresch, *Monatsh*, 1881, **2**, 277; Naff, *Annalen*, 1891, **265**, 113; Delepine, *Compt. rend.*, 1902, **134**, 1222; *Bull. soc. chim.*, 1861, *iii*, **27**, 814 ; Salkowski, *Ber.*, 1893, **26**, 2497), its formation by Hofmann's method appears to be the most satisfactory.

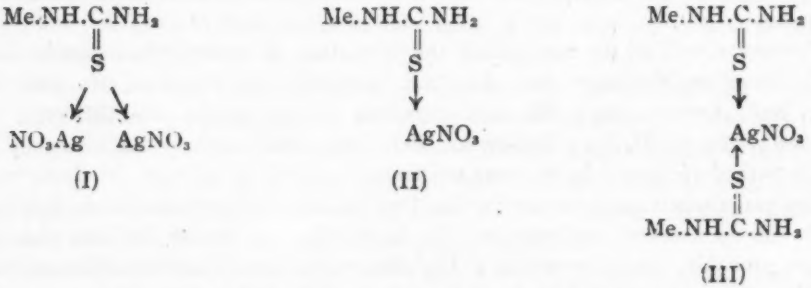
Our experiments on the isomerisation of methylamine thiocyanate to methylthiocarbamide and the isomeric conversion of the latter into the former indicate that these changes, probably, are not reversible in the conventional sense (vide Experimental, Table I). Absence in any considerable quantity of thiocyanic acid from the hydrolysate (*vide infra*) also points to the same conclusion. These results assume significance when viewed in the light of easy isomerisation of ammonium thiocyanate (Reynolds, *J. Chem. Soc.*, 1855, **7**, 1; Kappanna, this *Journal*, 1927, **4**, 217), hydrazine thiocyanate (Freund and Schander, *Ber.*, 1896, **29**, 2490) and aniline thiocyanate (this *Journal*, 1935, **12**, 629), although in the last case there is some doubt about the reversibility of the change. The compound is reported to melt at 118-19°. We were able to obtain under certain conditions crystals melting at 124° also. This is evidently due to dimorphism, a phenomenon not unusual in the chemistry of thiocarbamides.

Action of Hydrolytic Agents.—In contrast with phenylthiocarbamides (Krall *et al.*, this *Journal*, 1935, **12**, 635 *et seq*), the methylthiocarbamide is more easily decomposed by alkali than by acid. In this respect, as is expected by virtue of the presence of a positive substituent, its decomposition is more comparable with thiosemicarbazide (*ibid.*, 1941, **18**, 225; vide Experimental).

Desulphurisation.—Like aromatic thiocarbamides, the methylthiocarbamide is desulphurised with great ease by lead acetate, mercuric oxide, etc. (Dixon, *J. Chem. Soc.*, 1893, **63**, 318; Sahasrabudhey and Krall, this *Journal*, 1944, **21**, 63). Methylcyanamide is formed which is a volatile, pungent smelling liquid (Ainley, Curd and Rose, *J. Chem. Soc.*, 1949, 101). It was identified through its silver derivative which was found to agree with the composition $CH_3.NAg.CN$.

Action of Nitrous Acid.—As with thiocarbamide (Werner, *J. Chem. Soc.*, 1912, **101**, 2180; also this *Journal*, 1935, **12**, 640; 1951, **28**, 119), nitrous acid reacts initially to give the corresponding "formamidine disulphide" salt in a strong mineral acid medium. In presence of a weak acid, like acetic acid, nitrogen is evolved, but this reaction is slower in the present case as compared with thiocarbamide.

Reaction with Silver Nitrate.—Like thiocarbamide (Rathke, *Ber.*, 1881, **14**, 1774) and phenylthiocarbamide (Lal and Krall, this *Journal*, 1937, **14**, 474), methylthiocarbamide forms various complexes with silver nitrate in aqueous solutions (vide Table II). At ordinary temperatures with a moderate excess of $AgNO_3$ or in boiling solutions with a large excess, (I) is the principal product. At ordinary temperatures or in boiling solutions with an excess of methylthiocarbamide, (II) is the main product. Under other conditions (vide Experimental) mixtures of these result, and indeed, there is also some evidence of the formation of (III). In presence of a very large excess of silver nitrate no complex separates.



The complexes are stable only in presence of dilute nitric acid; in the absence of the latter desulphurisation occurs which is complete in boiling solutions (Cuthill and Atkins, *J. Soc. Chem. Ind.*, 1937, **56**, 57T). The complexes are formed with $AgNO_3$ molecules as a whole. Unlike, as in the case of reactions of cupric salts with phenylthiocarbamide, free acid is not liberated nor is any part of thiocarbamide oxidised. Silver thiocyanate also does not replace $AgNO_3$ from these complexes (cf. Lal and Krall, *loc. cit.*). Complexes are also formed with copper salts but these have not been examined in detail.

Oxidation.—On oxidation with various oxidising agents in an acidic medium, a salt of "formamidine disulphide" is obtained (Werner, *loc. cit.*). This also, most probably, has the monomeric structure, as has been shown for the oxidation products of thiocarbamide, NN-dimethylthiocarbamide (this *Journal*, 1952, **29**, 636) and tetramethylthiocarbamide (Sahasrabudhey, *loc. cit.*) and not the disulphide one as believed hitherto. This view finds support in the reaction of nitrous acid and also from the fact that when a mixture of methylthiocarbamide and thiocarbamide is oxidised, the oxidation product of thiocarbamide alone is obtained, a mixed disulphide does not result. In all its reactions, the oxidation product shows complete similarity with the oxidation products of other thiocarbamides.

Estimation of Methylthiocarbamide.—The interaction of aqueous methylthiocarbamide and iodine or mercuric nitrate can be used for the titrimetric estimation of the former (vide Experimental, Tables III and IV). In the case of iodine the dilution

limit and other considerations are very much similar to those with thiocarbamide (Reynolds and Werner, *J. Chem. Soc.*, 1903, **83**, 1; Werner, *ibid.*, 1912, **101**, 2166). The system

$$2Me.NH.C(=S).NH_2 + I_2 \rightleftarrows 2[Me.NH.C(=S).NH_2]I$$

is reversible like the system thiocarbamide—iodine and subject to, *mutatis mutandis*, similar influences.

Derivatives of Methylthiocarbamide.—On treatment with benzyl chloride and acetic anhydride in the usual way, a benzyl and an acetyl derivative are obtained which most probably have the following constitutions:

$$Me.NH.C(S.CH_2Ph)=NH \quad \text{and} \quad Me.N(CH_3CO)CS.NH_2$$

Experimental

Isomerisation

(a). *Isomerisation of Methylamine Thiocyanate to Methylthiocarbamide.*—Methylamine thiocyanate was prepared by adding equimolecular quantities of methylamine hydrochloride and potassium thiocyanate in alcohol. Potassium chloride formed was filtered out. To avoid decomposition and isomerisation, the solution was concentrated and crystallised under reduced pressure at ordinary temperature. After a second crystallisation the purity was confirmed by estimating the amine and thiocyanate content. The results of isomerisation carried out at 130° are shown in Table I.

Table I

Isomerisation of methylamine thiocyanate to methylthiocarbamide and vice versa.

Forward isomerisation (methylamine thiocyanate to methylthiocarbamide) at 130°. HCNS initially present in $MeNH_2$, HCNS taken = 15.6 c.c. $Hg(NO_3)_2$ soln.

Duration of heating.	Total $Hg(NO_3)_2$ equivalent after heating (% loss).	$MeNH_2$, HCNS after desulphurisation in terms of $Hg(NO_3)_2$ soln.	Unisomerised $MeNH_2$, HCNS.	$MeNH_2$, HCNS isomerised to MeNH. $CS.NH_2$.
1/2 hr.		15.2 c.c.	97.7 %	2.3 %
		15.3	98.0	2.0
1	15.3 c.c. (0.65 %)	—	—	—
	—	15.0	96.1	3.9
2	—	13.7	88.9	11.1
	—	13.7	88.9	11.1
3	—	12.3	79.8	20.2
	—	12.3	79.8	20.2
5	—	12.3	72.4	27.6
6	14.7 c.c. (4.6 %)	—	—	—
	—	9.6	62.3	37.7
	—	9.6	62.3	37.7
	—	9.0	57.7	42.3

Back isomerisation (methylthiocarbamide to methylamine thiocyanate) at 130°. Methylthiocarbamide initially present = 7.0 c.c. of $Hg(NO_3)_2$ soln.

Duration of heating.	Total $Hg(NO_3)_2$ equivalent after heating (% loss).	$MeNH_2$, HCNS after desulphurisation in terms of $Hg(NO_3)_2$ soln.	Unisomerised MeNH.$CS.NH_2$.	MeNH. $CS.NH_2$ isomerised to $MeNH_2$ HCNS.
1/2 hr.		0.3 c.c.	95.7 %	4.3 %
	—	0.25	96.4	3.6
1	7 c.c. (0 %)	—	—	—
	—	0.55	92.2	7.8
	—	0.45	93.6	6.4
2	—	1.0	85.7	14.3
	—	1.1	84.3	15.7
3	6.7 c.c. (4.3 %)	—	—	—
	—	1.30	81.4	18.6
4	—	1.55	77.9	22.1
	—	1.65	76.4	23.6
	—	1.55	77.9	22.1

(*b*) *Isomerisation of Methylthiocarbamide to Methylamine Thiocyanate.*—Methylthiocarbamide (0.1 g.) was weighed into several test tubes separately and heated in an oil-bath at 130° for different intervals. The results are presented in Table I.

The extent of conversion of methylamine thiocyanate into methylthiocarbamide and *vice versa* were found out by estimating the thiocyanate and thiocarbamide by mercuric nitrate, (*i*) directly and (*ii*) after desulphiding the methylthiocarbamide with alkaline cadmium sulphate. The method (*ii*) gave the quantity of thiocyanate and the difference between (*i*) and (*ii*) gave the quantity of thiocarbamide (vide Williams, "Cyanogen Compounds", p. 290).

Hydrolysis

Decomposition of methylthiocarbamide by boiling with acid and alkali of different strengths was investigated. The compound (0.9 g., 0.01 *M*) was treated under reflux with 25 c.c. of (*i*) *N*-H_2SO_4, (*ii*) *N*-NaOH, (*iii*) 5*N*-H_2SO_4 and (*iv*) 5*N*-NaOH. The resulting gases were passed through traps containing standard alkali in the case of (*i*) and (*iii*), and standard acid in the case of (*ii*) and (*iv*). No perceptible decomposition was observed in (*i*) and (*iii*). In (*ii*) and (*iv*), however, marked decomposition took place. The acid in the trap contained methylamine, and alkali hydrolysate gave the test for hydrogen sulphide. Amine was estimated by direct titration of the acid with a standard alkali, and by difference the amount of the same was calculated. The hydrogen sulphide was estimated iodometrically. With 1*N*-alkali, 14.2% amine and 5.2% H_2S and with 5*N*-alkali, 66.6% amine and 100% H_2S of the theoretical value were obtained.

Reaction with Silver Nitrate

The interaction of $AgNO_3$ with methylthiocarbamide has been investigated under different conditions. The details and results are recorded in Table II.

TABLE II

Interaction of methylthiocarbamide with silver nitrate.

No.	$CH_3NH.CS.NH_2$ taken.	$AgNO_3$ taken.	Molar ratio of $CH_3NH.CS.NH_2$ and $AgNO_3$.	Condition of experiments.	Complex taken for ignition.	Ag after ignition.	Ratio. Ag : loss on ignition.	Loss after ignition (NO_3 + $CH_3NH.CS.NH_2$)	Probable formula of the compound.
1	—	—	—	Ordinary temp.	1.3105 g.	0.6772 g.	(108 : 101)	0.6333 g.	Composition corresponds to $(AgNO_3)_2$, CSN_2H_3Me
2	—	—	—	,,	0.5280	0.2586	(108 : 112)	0.2694	
3	0.7898 g.	2.8720 g.	1 : 3	,,	0.9281	0.4586	(108 : 110)	0.4695	
4	0.8700	2.8720	1 : 2.7	,,	1.0060	0.4919	(108 : 112)	0.5141	
5	0.6131	0.5866	2 : 1	,,	0.1642	0.0611	(108 : 182)	0.1031	Corresponds to $AgNO_3$, CSN_2H_3Me with a slight (5-10%) of an higher complex, probably $AgNO_3$, $2CSN_2H_3Me$
6	0.7111	0.6466	2 : 1	Boiling soln.	0.2512	0.0913	(108 : 189)	0.1599	
7	0.4719	3.5282	1 : 4	Ordinary temp.	0.6212	0.2882	(108 : 125)	0.3330	
8	0.4650	3.5200	1 : 4	,,	0.7496	0.3327	(108 : 135)	0.4169	
9	0.4764	3.6266	1 : 4	Boiling soln.	0.6590	0.3135	(108 : 112)	0.3455	
10	0.4762	3.6266	1 : 4	,,	0.5179	0.2489	(108 : 116)	0.2690	Corresponds to $(AgNO_3)_2$, CSN_2H_3Me
11	0.90	0.20	8 : 1	Ordinary temp.	No ppt.				
12	1.80	0.40	8 : 1	,,	,,				
13	1.80	0.40	8 : 1	Boiling soln.	,,				

Oxidation

(*a*). *Oxidation of Methylthiocarbamide with Bromine.*—Finely powdered methylthiocarbamide (9 g.) was suspended in chloroform and bromine (8 g.) in chloroform was added to it in small lots, with vigorous stirring. A yellow mass separated when whole of the bromine solution was added, which was filtered and left under alcohol till its colour was discharged. It was crystallised from hydrobromic acid (dil.), m.p. 203° (decomp.). It gave a picrate, m.p. 130°.

Its reaction with aqueous KI is analogous to formamidine disulphide. The iodine liberating capacity of this hydrobromide was determined under the influence of various factors: Iodine liberation increased with increasing concentration of KI and acidity, and decreased with increasing dilution and concentration of methylthiocarbamide.

(*b*). *Mixed Oxidation of Methylthiocarbamide and Thiocarbamide.*—Methylthiocarbamide (0.45 g.) and thiocarbamide (0.38 g.) were taken in a 400 c.c. beaker and dissolved in 20 c.c. water. The solution was acidified with 4 c.c of 5*N*-H_2SO_4, and further diluted with 20 c.c. water. *N*-$NaNO_2$ solution (8 c.c.), diluted to 20 c.c., was added dropwise with constant stirring. Excess of picric acid was added to this solution till there was no further precipitation. The precipitated picrate was filtered, dried and weighed on a tared filter paper. Its m.p. was found to be 152-54°. (Found: picrate, 1.4878 g. Calc. from thiocarbamide, 1.5250 g.). The experiment clearly indicates that a mixed derivative is not formed.

Estimation of Methylthiocarbamide

(*a*). *With Iodine Solution.*—Methylthiocarbamide was titrated with *N*/10-iodine solution directly at different dilutions using starch as the indicator; 0.02% solution gave quantitative results.

TABLE III

Estimation of methylthiocarbamide with iodine.

Methylthiocarbamide soln. (0.9 g./100 c.c.) = 5 c.c.

Water added.	Total bulk.	*N*/10-I_2 soln.	Water added.	Total bulk.	*N*/10-I_2 soln.	Water added.	Total bulk.	*N*/10-I_2 soln.
0 c.c	5 c.c.	2.00 c c.	40 c.c.	45 c.c.	3.20 c.c.	157 c.c.	162 c.c.	4.65 c c.
5	10	2.15	80	85	3.60	177	182	* 5.00
10	15	2.65	137	142	4.20	207	212	5.00
20	25	2.75				237	242	5.00

* This is also the theoretically calculated quantity.

(*b*). *With Mercuric Nitrate Solution.*—Methylthiocarbamide can be volumetrically estimated by titration against standard mercuric nitrate solution using ferric alum as an indicator. Results are presented in Table IV.

TABLE IV

Estimation of methylthiocarbamide with mercuric nitrate.

Stock soln. (0.9 g./100 c.c.) = 10 c.c.

KCNS soln. added.	Water added.	Total bulk.	$Hg(NO_3)_2$ for KCNS + methyl thiocarb.	$Hg(NO_3)_2$ for KCNS alone.	$Hg(NO_3)_2$ for methyl-thiocarb. alone
1 c.c.	0 c.c.	11 c.c.	8.5 c.c.	0.95 c.c.	7.55 c.c.
1	40	51	8.5	0.95	7.55
1	90	101	8.5	0.95	7.55
5	0	15	12.1	4.6	7.50
5	35	50	12.1	4.6	7.50
5	85	100	12.15	4.6	7.55
20	0	30	26.20	18.7	7.50
20	70	100	26.25	18.7	7.55

10 c. c. of thiocarbamide solution theoretically require 7.55 c.c. of $Hg(NO_3)_2$.

Interaction with Acetic Anhydride and Benzyl Chloride

(*a*) N-*Acetyl Derivative.*—Methylthiocarbamide (5 g.) and acetic anhydride (10 c.c.) were heated under reflux for about 15 minutes. The mass was poured in a beaker containing 50 c.c. water. The solid separating was crystallised from water, m.p. 173°. (Found: N, 21.0; S, 24.3. Calc. for $C_4H_8ON_2S$: N, 21.2; S, 24.2 per cent).

(b) S-*Benzyl Derivative.*—Equimolecular quantities of benzyl chloride and methylthiocarbamide were warmed in 40% alcohol. After evaporating the solvent a sticky solid mass was left behind. It was dissolved in water and picric acid was added to it. Yellow crystalline mass separated, which after crystallising from alcohol melted at 185°. (Found: S, 7.7. Calc. for $C_{15}H_{13}N_5O_7S$: S, 7.8 per cent).

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STUDIES ON THE SOLUBILITY AND LIGHT FASTNESS OF AZO DYES. PART III

By A. B. Sen and R. C. Sharma

Thirty new azo dyes have been prepared from *m*- and *p*-aminoacetophenones with a view to studying their solubility and fastness to light. The colour of these dyes in finely powdered state has been standardised according to Lovibonds' colour nomenclature.

The effect of various substituents on solubility and light fastness has also been studied.

A survey of the literature reveals that only a few azo dyes have so far been obtained from *m*- and *p*- aminoacetophenones (Hewitt, Mann and Pope, *J. Chem. Soc.*, 1914, **105**, 2195, 2197, 2199, 2202). We have now prepared thirty new azo dyes from these two amines with a view to studying their solubility and light fastness and the influence which the -$COCH_3$ group (when present in the amino part of the dye molecule) exerts on these properties. The solubility and stability towards sunlight were determined by following the methods described in the earlier papers of this series (this *Journal*, 1951, **28**, 657 ; 1952, **29**, 931).

These dyes were characterised through their acetates and their colours were standardised with a Lovibond tintometer.

Experimental

Preparation of Azo Dyes (*Dye No.* 1).—*m*-Aminoacetophenone (2 g.) was dissolved in 5.4 c.c. of 50% HCl and the ice-cold solution was diazotised with sodium nitrite (1.18 g.), dissolved in ice-cold water. The diazonium salt was then coupled with phenol (1.41 g.), dissolved in caustic soda solution (1.18 g. of alkali in 10 c.c. H_2O). After allowing it to stand for an hour, the sodium salt was decomposed with HCl and the dye obtained was recrystallised from alcohol, yield 3.42 g. (96%).

Other dyes of this series were prepared in a similar way. Acetates of these dyes were also prepared for their characterisation in the usual way. The details of the compounds obtained are given in Tables Ia and Ib.

The dyes were finely powdered and sieved through a standard gauze of 0.25 mesh. A Lovibond tintometer was used for the standardisation of the colour of the powders, strictly adhering to the technique suggested for this purpose. Table IIa and IIb give the colours of the dyes recorded according to Lovibonds' colour nomenclature.

TABLE Ia

Dyes from m-*aminoacetophenone.*

A stands for acetophenone-*m*-azo-

Sr. No.	Dye.	M.p.	Amt. of dye from 2 g. of amine.	Yield.	Nitrogen Calc.	Nitrogen Found.	M.p. of acetate.	Nitrogen Calc.	Nitrogen Found.
1.	A-phenol†	166°	3.42 g.	96.0%	11.66%	11.86%	128°	9.93%	10.04%
2.	A-*o*-chlorophenol†	182°	3.98	98.0	10.20	10.01	82°	8.84	9.08
3.	A-*p*-chlorophenol*	132°	4.0	98.5	10.20	10.42	84°	8.84	8.62
4.	A-2:4-dichlorophenol*	170°	4.5	98.0	9.93	9.08	120°	7.95	8.05
5.	A-*o*-cresol†	148°	3.6	95.7	11.02	10.85	75°	9.24	9.16
6.	A-*m*-cresol†	150°	3.7	98.4	11.02	10.84	70°	9.24	9.22
7.	A-1:4:5-xylenol*	158°	3.8	94.2	10.44	10.38	89°	9.03	8.96
8.	A-*m*-ethylphenol†	142°	3.8	94.2	10.44	10.40	—	—	—
9.	A-3:5-ethylmethylphenol†	122°	4.0	96.0	9.93	10.12	78°	8.63	8.83
10.	A-*m*-salicylaldehyde*	164°	3.8	94.2	10.44	10.60	132°	9.03	9.06
11.	A-resorcinol*	181°	3.5	92.6	10.93	11.02	112°	8.24	8.40
12.	A-*o*-hydroxydiphenyl*	155°	4.5	96.2	8.86	8.84	89°	7.82	7.60
13.	A-*p*-hydroxydiphenyl*	120°	4.5	96.2	8.86	8.62	153°	7.82	7.92
14.	A-*p*-*tert.*-butylphenol†	108°	4.0	91.3	9.45	9.48	124°	8 05	8 86
15.	A-*p*-*tert* -amylphenol†	72°	3.5	76.3	9.03	9.58	55°	7.95	8.01

TABLE Ib

Dyes derived from p-*aminoacetophenone.*

A stands for acetophenone-*p*-azo-.

Sr. No.	Dye.	M.p.	Amt. of dye from 2 g. of amine.	Yield.	Nitrogen Calc.	Nitrogen Found	M.p. of acetate.	Nitrogen Calc.	Nitrogen Found.
16.	A-*o*-chlorophenol†	172°	4.0 g.	98.5%	10.20%	10.42%	89°	8.84%	9.03%
17.	A-*p*-chlorophenol†	136°	4.0	98.5	10.20	10.40	102°	8.84	8.62
18.	A-*o*-cresol†	168°	3.6	95.7	11.02	11.32	126°	9.24	8.85
19.	A-*m*-cresol†	120°	3 7	98 4	11.02	10.92	96°	9.24	9.44
20.	A-1:3:4-xylenol†	110°	3.9	98.3	10.44	10.82	104°	9.03	9.42
21.	A-1:4:5-xylenol†	140°	3.9	98.3	10.44	10.80	134°	9.03	8.78
22.	A-*m*-ethylphenol*	117°	3·8	94.2	10.44	10.12	141°	9.03	8.82
23.	A-3:5-ethylmethylphenol†	132°	4 0	96.0	9.93	10.13	64°	8.64	8.15
24.	A-*o*-nitrophenol†	140°	3.8	90.1	14.73	14.98	105°	12.54	12.08
25.	A-*m*-nitrophenol*	225°.	4 0	92.7	14.73	14.56	114°	12.54	12.50
26.	A-salicylaldehyde†	170°	3.8	94 2	10.44	10.64	135°	9.03	0.42
27.	A-*o*-hydroxydiphenyl†	162°	4.5	96.2	8.86	8.95	189°	7 82	8.02
28.	A-*p*-hydroxydiphenyl*	158°	4.0	98 3	8.86	9.24	112°	7.82	7.66
29.	A-*p*-*tert.*-butylphenol†	122°	4.0	91.3	9.45	9.25	158°	8 05	8.08
30.	A-*tert.*-amylphenol†	87°	4 0	87.2	9.03	8.85	85°	7.95	8.05

† Dyes recrystallised from alcohol.

* Dyes recrystallised from glacial acetic acid.

TABLE IIA

Colour of the dyes.

Sr. No.	Matching standards			Colour developed		
	Red.	Yellow.	Blue.	Amt. of neutral tint (grey).	Component colour.	Predominating colour.
1.	4	10.9	—	—	Orange 4	Yellow 6.9
2.	4	10.1	—	—	Orange 4	Yellow 6.1
3.	5.4	20	2	2	Orange 3.4	Yellow 14.6
4.	5.3	20	1	1	Orange 4.3	Yellow 14 7
5.	8	24	—	—	Orange 8	Yellow 16
6.	4	20	—	—	Orange 4	Yellow 16
7.	7.2	20	3	3	Orange 4.2	Yellow 12.8
8.	5.5	20	—	—	Orange 5.5	Yellow 14.5
9.	7.5	20	—	—	Orange 7.5	Yellow 12.5
10.	2.4	20	—	—	Orange 2.4	Yellow 17.6
11.	9.3	20	5	5	Orange 4.3	Yellow 10.7
12.	5.5	20	1	1	Orange 4.3	Yellow 14.5
13.	4.7	20	—	—	Orange 4.7	Yellow 15.3
14.	7	23.7	—	—	Orange 7	Yellow 16.7
15.	9.8	29.8	4	4	Orange 5.8	Yellow 20

TABLE IIB

Colour of the dyes.

Sr. No.	Matching standards			Colour developed		
	Red.	Yellow.	Blue.	Amt. of neutral tint. (Grey).	Component colour	Predominating colour.
16.	6.5	22	—	—	Orange 6.5	Yellow 15.5
17.	9	24	—	—	Orange 9	Yellow 15
18.	8.4	29	—	—	Oronge 8.4	Yellow 20.6
19.	20	7	—	—	Orange 7	Red 13
20.	8.5	22	4	4	Orange 4.5	Yellow 13.5
21.	8.3	22	2	2	Orange 6.3	Yellow 13.7
22.	9.5	20.9	4.3	4.3	Orange 5.2	Yellow 20.4
23.	13	6	4	4	Orange 2	Red 7
24.	8.1	22	3	3	Orange 5.1	Yellow 13.9
25.	9	23	1	1	Orange 8	Yellow 14
26.	8	20	2.2	2.2	Orange 5.8	Yellow 12
27.	7.3	28	4.4	4.4	Orange 2.9	Yellow 20 7
28.	9	23	2	2	Orange 7	Yellow 14
29.	9.4	27	1	1	Orange 8.4	Yellow 17.6
30.	17	6	4	4	Orange 2	Red 11

Serial numbers of the dyes in Tables IIA and IIB correspond to those in Tables IA and IB.

Solubility Determination.—Solubility of only nine dyes (selected on the basis of groupings expected to confer lipoid solubility) was determined in anhydrous benzene, 95% alcohol and groundnut oil, following the methods already described in previous communications (*loc. cit.*). Results obtained are shown in Table III.

TABLE III

Sr. No.	Dye No.	Solubility in 100 g. of solvent at 30° in		
		Alcohol.	Benzene.	Oil.
I	8	8.5 g.	0.86 g.	0.958 g.
II	9	9.1	9.35	1.565
III	7	4.0	1.25	1.365
IV	13	1.86	6.11	0.884
V	19	0.61	11.78	1.565
VI	22	30.8	6.9	1.20
VII	20	1.60	11.82	1.02
VIII	30	2.85	11.83	6.21
IX	17	0.0932	2.56	0.229

Fastness to Light.—The stability of the above dyes towards sunlight was also studied by exposing approximately 0.1% solutions in groundnut oil to the sun for 20 days (May-June). The amount of fading was determined with the help of Klett-Summerson photoelectric colorimeter (cf. this *Journal*, 1951, **28**, 657). Results obtained are shown in Table IV.

TABLE IV

Sr. No.	Dye No.	Initial col. reading.	Conc.	Col. reading after exposure.	Fading.
I	8	10	0.0997%	7	30%
II	9	12	0.082	9	25
III	7	15	0.0976	9	40
IV	13	20	0.0855	5	75
V	19	34.5	0.0999	24	30.15
VI	22	9	0.070_2	6	33 3
VII	20	36	0.0840	12	66.6
VIII	30	8	0.0702	3	62.4
IX	17	27	0.0813	18	33.3

CONCLUSION

From the results obtained it is found that the introduction of $-COCH_3$ group in the amino part of the dye molecule decreases the solubility in benzene as well as in groundnut oil. Data on dyes No. 9, 19, 22 and 30, as compared with our previous results (*loc. cit.*), reveal this fact.

Light fastness of the dyes is also not appreciably improved by this group. In general, the introduction of the $-COCH_3$ group renders the dyes more fugitive to sunlight (cf. Table IV) and less soluble in benzene and oil (cf. Table III).

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STUDIES IN THE BEHAVIOUR OF BI-UNIVALENT SALTS IN AQUEOUS SOLUTION. PART VI. MERCURIC ACETATE

By P. Mahapatra, S. Aditya and B. Prasad

From the measurement of solubility of mercuric oxide (red) in solution containing sodium acetate and acetic acid, mercuric acetate in solution is shown very little to dissociate. It exists in the form $Hg(CH_3COO)_2$ (undissociated). The equilibrium constant K for $Hg(CH_3COO)_2 \rightleftarrows Hg^{++}+2CH_3COO^-$ has been calculated to be 3.75×10^{-9}.

Mercuric acetate dissociates to a small extent (Sidgwick, "Chemical Elements and their Compounds", p 325). Literature does not record any attempt to determine the degree of dissociation of mercuric acetate. The present investigation has been attempted to obtain a quantitative idea about the nature of ion or molecular species that might be present in aqueous solution of mercuric acetate. A method similar to that adopted by Edmonds and Birnbaum (*J. Amer. Chem. Soc.*, 1940, **62**, 2367) for the study of the nature of lead acetate in solution has been followed. The solubility of mercuric oxide (red) has been studied in solution containing different amounts of acetate and acetic acid.

Experimental

Merck's extra pure mercuric oxide (red) was used for the work. Acetic acid solution was prepared from the glacial acetic acid, purified by freezing an extra pure sample. Caustic soda solution from pure caustic soda was prepared and standardised with pure succinic acid. The acetic acid solution was standardised with the caustic soda solution. To get the various solutions, required volumes of caustic soda and acetic acid solutions of known concentrations were taken and then made to a definite volume.

Solubility Determination.—For each experiment two r. b. Pyrex flasks, cleaned and dried, were taken. To each was added 100 c.c. solution of known strength of acetic acid and sodium acetate and to that was added about 5 to 7 g. of mercuric oxide. The flasks with their contents were shaken in a mechanical shaker for about five days and then put in a water thermostat for nearly the same length of time with occasional shaking. The flasks were taken out and the solution in each was analysed for the concentration of mercury by iodate method (Lang, "Newer Methods of Volumetric Analysis", Trans. by Oesper, p. 97). The titre value of the duplicate experiments agreed within a drop. As the shaking was done at 25°-30°, the thermostat temperature was 35° and

as the solubility of mercuric oxide decreased with temperature, which was seen in preliminary experiments, there was no doubt about the attainment of equilibrium. The agreement between the solubility results obtained in duplicate experiments (even when the two flasks kept in the thermostat for different lengths of time) justifies the fact that equilibrium was attained in each case. These results are shown below with the calculated figures.

TABLE I

$[NaAc]_0$.	$[HAc]_0$.	$[Hg]_{Total}$.	$[HAc]_f$.	$[NaAc]_0$.	$[HAc]_0$.	$[Hg]_{Total}$.	$[HAc]_f$.
0.50 *M*	0.50 *M*	0.1864 *M*	0.1273 *M*	0.10 *M*	1.00 *M*	0.0287 *M*	0.0426 *M*
0.25	0.25	0 0800	0 0900	0.50	0.05	0.0098	0 0304
0.125	0.125	0.03757	0.0534	0.25	0.025	0 00296	0.0191
0.10	0.10	0.0283	0.0434	0.04	0.32	0 1081	0.1040
				0.02	0.16	0.0481	0 0640
0.0625	0.0625	0.01636	0.0301	0.01	0.08	0.0198	0.0400
0.05	0.05	0.01227	0.0254				
0.04	0.04	0.0089	0.0220	1.00	0.5	0 2054	0 0802
0.0625	0 25	0.0690	0.0960	0.50	0 25	0.08095	0.0880
0.05	0.20	0.0663	0.0677	0.25	0.125	0 0357	0 0536
0.04	0.16	0.0488	0.0624	0.125	0 062	0 0162	0.0301
0.02	0.08	0.0200	0.0400	0.100	0.050	0.00968	0.0306
0.010	0.04	0.0083	0.0234	0.0625	0.03125	0 00628	0.0186
				0.05	0.0250	0 005095	0.0159
0.10	0 20	0.0674	0.0650				
0.625	0.125	0 03757	0.0490	0.50	0.100	0.0266	0.0468
0.05	0.10	0.0277	0.0446	0.25	0.05	0.01104	0.0280
0.04	0.08	0.0192	0.0420	0.125	0.025	0.005065	0.01490
0.02	0.04	0.0084	0.0233	0.10	0.020	0.003863	0.01230
0.01	0.02	0 0034	0.0132				

DISCUSSION

The equilibrium of Hg^{++} in solution will be roughly controlled by

$$[Hg^{++}][OH^-]^2 = K_s \quad \ldots \quad \ldots \quad (1)$$

For more accurate calculations, concentrations have to be replaced by activities.

The best value of solubility product of mercuric oxide is taken to be 4×10^{-26} (Allmond, *Z. Elektrochem.*, 1904, **10**, 880). This is the value accepted by Garret and Hirchler (*J. Amer. Chem. Soc.*, 1938, **60**, 299).

$$\text{So} \qquad [Hg^{++}] = \frac{K_s}{[OH]^2} = \frac{4 \times 10^{-26}}{[OH]^2} \quad \ldots \quad \ldots \quad (2)$$

Further, in the case of acetic acid

$$\frac{[H^+][Ac^-]}{[HAc]} = 1.8 \times 10^{-5} \quad \ldots \quad \ldots \quad (3)$$

Taking K_w (ionic product of water) to be 1.0×10^{-14}, it follows from equations (2) and (3) that

$$[Hg^{++}] = \frac{K_s K_a^2}{K_w^2} \frac{[Ac^-]^2}{[HAc]^2} = \frac{4 \times 10^{-26} \times (1.8)^2}{[Ac^-]^2/[HAc]^2} \quad \ldots \quad \ldots \quad (4)$$

So, in order to find out the concentration of Hg^{++}, the ratio of the concentration of salt to that of acid at equilibrium is required. Let us assume that $Hg(OH)_2$ reacts with acetic acid according to the scheme,

$$Hg(OH)_2 + 2HAc \longrightarrow HgAc^+ + 2H_2O + Ac^-$$
$$\uparrow\downarrow$$
$$Hg^{++} + Ac^-$$

If nearly all the mercury in solution remains as $HgAc^+$, the increase in the amount of acetate ion would be equal to the number of moles of $HgAc^+$ formed, which is equal to the number of gram atoms of mercury in solution. Therefore, the total amount of acetate ions in the solution at equilibrium would be equal to the gram mole of sodium acetate taken plus the number of gram atoms of mercury in solution, *i.e.*,

$$[Ac^-]_{final} = [Ac^-]_{Initial} + [Hg]_{total} \quad \ldots \quad \ldots \quad (5)$$

For every molecule of mercuric oxide, which goes into solution, two molecules of acetic acid are used up. So the concentration of acetic acid at equilibrium is decreased and is given by

$$[HAc]_{f(final)} = [HAc]_{0(Initial)} - \frac{\text{g. mole of acetic acid consumed}}{\text{volume of the solution}}$$
$$= [HAc]_0 - 2[Hg]_{T(total)} \quad \ldots \quad \ldots \quad (6)$$

where $[HAc]_0$ and $[HAc]_f$ are original and final concentrations of acetic acid in solution.

The equation (4) can be written as,

$$[Hg^{++}] = \frac{K_s K_a^2}{K_w^2 \left[\frac{[Ac]_0 + [Hg]_T}{[HA]_{Initial} - 2[Hg]_T}\right]^2} \quad \ldots \quad \ldots \quad (7)$$

Now for the equilibrium $HgAc^+ \underset{\text{almost complete}}{\overset{\text{negligible}}{\rightleftharpoons}} Hg^{++} + Ac^-$, we have

$$K = \frac{[Hg^{++}]\,[Ac^-]}{[HgAc^+]}$$

or $\log [Ac^-]_{final} = \log [HgAc^+] - \log [Hg^{++}] + \log K \quad \ldots \quad \ldots \quad (8)$

The $[Hg^{++}]$ is so small in comparison with $[Hg]_{T(total)}$, that we may take $[HgAc^+] = [Hg]_T$; so the equation (8) reduces to

$$\log [Ac^-]_{final} = \log [Hg]_T^2 - \log [Hg^{++}] + \log K \quad \ldots \quad \ldots \quad (8A)$$

Now $\log [Ac^-]_{final}$ is calculated from equation (5); $\log [Hg]_T$ is taken from the estimated value and $\log [Hg^{++}]$ is calculated from equation (7). If $\log [Ac^-]_{final}$ is plotted against $\log [Hg]_T - \log [Hg^{++}]$, the slope should be equal to unity, as seen from (8A), but actually it is found to be about 0.5. So the above picture of machanism of dissociation is not correct.

Let us take another picture,

$$Hg(OH)_2 + 2HAc \rightleftharpoons HgAc_2 + 2H_2O$$
$$\text{negligible}\ \downarrow\uparrow\ \text{almost complete}$$
$$Hg^{++} + 2Ac^-$$

In this picture the final concentration of the acetate ion at equilibrium remains the same as the initial stage, *i. e.*, $[Ac^-]_f = [Ac^-]_0$. But the amount of acetic acid is decreased by twice the number of gram moles of mercuric oxide dissolved.

Therefore $$[HAc]_f = [HAc]_0 - 2[Hg]_T \quad \ldots \quad \ldots \quad \ldots \quad (9)$$

In Table I, columns 2 and 6 give the initial concentration of acetic acid, columns 3 and 7, the total concentration of mercury in the solution, columns 4 and 8, the final concentration of acetic acid calculated by equation (9). So from equation (9) the concentration of mercuric ion $[Hg^{++}]$ comes out as follows,

$$[Hg^{++}] = \frac{K_2 \times K_a^2}{K_w^2 \left[\frac{[Ac^-]_0}{[HAc]_0 - 2[Hg]_T}\right]^2} \quad \ldots \quad \ldots \quad (10)$$

Further, $$[Hg]_T = [Hg^{++}] + [HgAc_2].$$

Since the amount of $[Hg^{++}]$ as calculated from equation (10) is negligible as compared to $[Hg]_T$, we can write $[Hg]_T = [HgAc_2]$ except when their difference is required.

The product K of the equilibrium constants K_1 and K_2 ($HgAc_2 \rightleftarrows HgAc^+ + Ac^-$, K_1; $HgAc^+ \rightleftarrows Hg^{++} + Ac^-$, K_2) corresponds to the equilibrium

$$HgAc_2 \rightleftarrows Hg^{++} + 2Ac^-$$

where $$K = \frac{[Hg^{++}]\,[Ac^-]^2}{[HgAc_2]} = \frac{[Hg^{++}][Ac^-]_0^2}{[Hg]_T}$$

because $[Ac^-]_f = [Ac^-]_0$ and $[HgAc_2] = [Hg]_T$, as shown above;

or $$\log [Ac^-]_0 = \tfrac{1}{2}\{\log [Hg]_T - \log [Hg^{++}]\} + \tfrac{1}{2} \log K \quad \ldots \quad \ldots \quad (11)$$

When $\log [Ac^-]_0$ is plotted against $\{\log[Hg]_T - \log [Hg^{++}]\}$, the slope is found to be 0.5, which agrees with the requirement of the equation.

The intercept, when $\{\log [Hg_T] - \log [Hg^{++}]\}$ is zero, gives the value of $\frac{1}{2} \log K$.

The graph gives for the intercept a value of -4.25, so that $-\log K = \bar{9}.5$ or $K = 3.16 \times 10^{-9}$. This definitely gives a support to the view that mercuric acetate in solution exists in undissociated state.

In the above calculations no account of the interionic attraction has been taken. It can be taken into account as shown below.

For equilibrium $HgAc_2 \rightleftarrows Hg^{++} + 2Ac^-$,

$$K = \frac{(Hg^{++})\,(Ac^-)^2}{(HgAc_2)},$$

where ( ) denotes activity. So K is the thermodynamic dissociation constant.

But $(Hg^{++})\ (OH^-)^2 = K_s$, where K_s is the solubility product of mercuric oxide in water. Replacing (Hg^{++}) by $K_s/(OH^-)^2$ in the above equation it becomes,

$$K = \frac{K_s \times (Ac^-)^2}{(OH^-)^2 (HgAc_2)}$$

or
$$K = \frac{K_s (H^+)^2 - (Ac^-)^2}{K_w^2\ (HgAc_2)}\ , \text{ where } K_w = (H^+)\ (OH^-).$$

Moreover, in the solution $\frac{(H^+)\ (Ac^-)}{(HAc)}\ K_a$ is to be satisfied.

So
$$K = \frac{K_s\ K_a^2\ (HAc)^2\ (Ac^-)^2}{K_w^2\ (Ac^-)^2\ (HgAc_2)}$$

or
$$\frac{(HAc)^2}{(HgAc_2)} = \frac{K \times K_w^2}{K_s \times K_a}$$

since the acetic acid and mercuric acetate are undissociated, their activity coefficient may be taken to be unity.

Taking logarithm,

$$\log\ [HAc]_f = \tfrac{1}{2}\ \log \frac{K \times K_w^2}{K_s \times K_a^2} - \tfrac{1}{2}\ \log\ [HgAc_2].$$

The values of $[HAc]_f$ and $[Hg]_T$ are given in Table I. As already explained, $[HgAc_2]$ may be taken to be equal to $[Hg]_T$. When log $[HAc]$ is plotted against log $[Hg]_T$, the slope is 0.5 and the intercept is -0.45. From this, the value of K comes to 3.75×10^{-8}. This value of K is more accurate as in this case the interionic attraction has been accounted for.

This K, as already explained, is equal to K_1K_2. Since most of the mercuric acetate is in undissociated form, the dissociation of both the stages must be very small.

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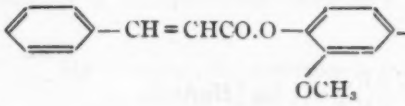
CHEMICAL EXAMINATION OF *PICRORHIZA KURROOA*, BENTH. PART II. ATTEMPTED SYNTHESIS OF KUTKIN

By R. P. Rastogi and A. B. Sen

1-Tetra-acetylglucosido-4-cinnamoylvanillate has been synthesised by the condensation of cinnamoylvanillic acid and acetobromoglucose, which on deacetylation is split into cinnamamide and 1-β-D-glucosidovanillate. 1-Tetra-acetylglucosido-4-cinnamoylvanillate gives a depression in melting point on admixture with acetylkutkin.

Rastogi, Sharma and Siddiqui (*J. Sci. Ind. Res.*, 1949, **8B**, 173) reported the isolation of a bitter glucoside, kutkin ($C_{23}H_{28}O_{12}$), from the roots of *Picrorhiza kurrooa* and as the glucoside gave cinnamic acid, vanillic acid and glucose on alkaline hydrolysis, they tentatively assigned the following (1-β-D-glucosido-4-cinnamoylvanillate) structure to it :

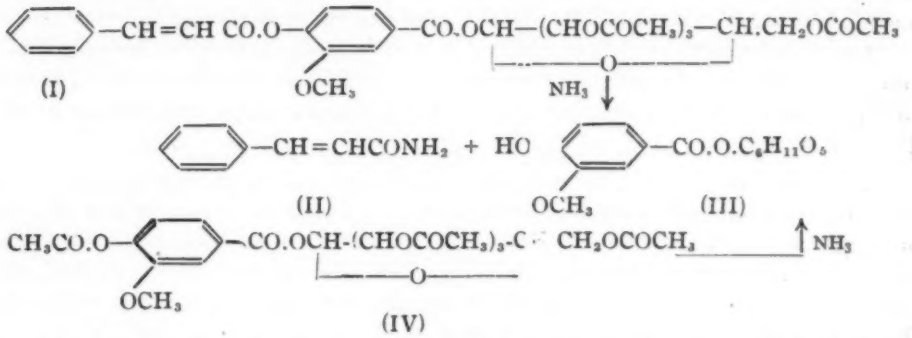


The apparent discrepancy between the molecular formulae of 1-β-D-glucosido-4-cinnamoylvanillate ($C_{23}H_{24}O_{10}$) and that of kutkin ($C_{23}H_{28}O_{12}$) is regarded to be due to the presence of two molecules of water of crystallisation in kutkin which are not removable even at 100° in vacuo. Since this appeared to be the first instance of a naturally occurring glucose ester of an aglucone consisting of two different acids, and in view of the apparent discrepancy mentioned above, it was considered desirable to undertake a synthesis of 1-β-D-glucosido-4-cinnamoylvanillate, in order to verify the structure of kutkin.

Cinnamoylvanillic acid was synthesised (*a*) through the condensation of cinnamoyl chloride with vanillic acid and (*b*) by the condensation of cinnamoyl chloride with vanillin, followed by oxidation of the cinnamoylvanillin with silver oxide in aqueous solution. A third alternative method attempted was through the carbonation of the Grignard compound of 5-bromocinnamoylguaiacol which, however, was not successful because of the inability of the bromo compound to form the corresponding magnesium or lithium compound.

Condensation of cinnamoylvanillic acid with acetobromoglucose in presence of silver oxide in dry quinoline (Robertson and Waters, *J. Chem. Soc.*, 1930, 2729) gave the crystalline 1-tetra-acetylglucosido-4-cinnamoylvanillate (I) in 87% yield. An identical product was also obtained by the condensation of the silver salt of cinnamoylvanillic acid and acetobromoglucose in xylene, but the yield of (I) was only 22%. The authenticity of this compound was established through its hydrolysis and subsequent identification of cinnamic and vanillic acids and glucose in the hydrolysate through paper chromatography.

Deacetylation of (I) was carried out with methanolic ammonia at 0°. Instead, however, of the expected compound (1-β-*D*-glucosidocinnamoylvanillate), the resultant mixture was found to consist of cinnamamide (II) and 1-β-*D*-glucosidovanillate (III) formed due, apparently, to the fission of the molecule, followed by the condensation of the liberated cinnamic acid with ammonia. The identity of 1-β-*D*-glucosidovanillate was established through analytical data and paper chromatography of its hydrolysate and was confirmed through the mixed melting point with an authentic sample, prepared by deacetylation of the condensation product of acetylvanillic acid and acetobromoglucose.



Due to the fission of (I) during the process of deacetylation, as mentioned above, a comparison of the melting and the mixed melting points of kutkin with the synthetic 1-β-*D*-glucosido-4-cinnamoylvanillate could not be made. However, a mixture of the acetylglucosidocinnamoylvanillate (m. p. 158°) with acetylkutkin (m.p. 180°) melted at 147°, showing that these two products are not identical. It would thus appear that the tentative formula for kutkin, proposed by Rastogi, Sharma and Siddiqui (*loc. cit.*), would require modification. Further work in this direction is in progress.

EXPERIMENTAL

Cinnamoylvanillic Acid

(*a*). *Condensation of Cinnamoyl Chloride with Vanillic Acid.*—Vanillic acid (10 g.) and cinnamoyl chloride (12.5 g.) were refluxed together in dry benzene (40 c.c.) for 3 hours. The benzene solution was washed free of acid, dried over anhydrous sodium sulphate and freed of the solvent. The residue on crystallisation from hot alcohol gave colorless needles, m.p. 196°, yield 6.5 g. It is soluble in acetone and ethyl acetate, fairly so in ether, and insoluble in benzene and alcohol. [Found : C, 67.9 ; H, 4.8 ; M.W. (Rast), 305. $C_{17}H_{14}O_5$ requires C, 68.4 ; H, 4.7 per cent. M.W., 298].

(*b*). *Condensation of Vanillin with Cinnamoyl Chloride and Oxidation of the Resultant Product.*—Vanillin (5 g.) and cinnamoyl chloride (6 g.) were refluxed together in dry benzene solution for 3 hours on a water-bath. The reaction mixture was washed free of hydrochloric acid, dried over anhydrous sodium sulphate and freed of the solvent. The residue was dissolved in alcohol, filtered, made turbid with water and left in the refrigerator for crystallisation. The thick deposit of colorless needles of

cinnamoylvanillin, thus obtained, was filtered and recrystallised from dilute alcohol, m.p. 81°, b.p. 130-35°/2 mm., yield 5.9 g. It is soluble in alcohol, acetone and benzene and insoluble in petroleum ether. (Found: C, 72.0; H, 5.11. $C_{17}H_{14}O_4$ requires C, 72.3; H, 4.9 per cent).

Cinnamoylvanillin (5 g.) and freshly precipitated silver oxide (10 g.) were suspended in water (100 c.c.) and heated with stirring on a water-bath for 4 hours. The reaction mixture was acidified and extracted with ethyl acetate. The ethyl acetate layer was washed free of acid, dried over anhydrous sodium sulphate and freed of the solvent. The residue on crystallisation from hot alcohol gave colorless needles, m.p. 196°, yield 3.2 g. which are identical with the product obtained by the procedure (*a*).

(*c*). *Condensation of 5-Bromoguaiacol with Cinnamoyl Chloride.*—5-Bromoguaiacol was prepared by dropwise addition of bromine into a cooled and stirred solution of guaiacol in dry carbon tetrachloride, m.p. 45° (*Chem. Abst.*, 1899, II, 1079; Hoffmann La Roche Co., D.R.P. 105052).

5-Bromoguaiacol (10 g.), cinnamoyl chloride (10 g.) and magnesium (0.5 g.) were refluxed on a water-bath in dry benzene for 2 hours. The reaction mixture was diluted with ether, decanted, washed with water, dilute caustic soda solution and finally again with water. It was dried over anhydrous sodium sulphate and the solvent distilled off. The residue crystallised from hot alcohol as needles, m.p. 111°, yield 10.5 g. (Found: Br, 23.4. $C_{16}H_{13}O_3$ requires Br, 23.0 per cent).

All attempts to prepare the magnesium or the lithium derivatives of cinnamoylguaiacol proved unsuccessful, and thus, the carbonation could not be carried out.

Hydrolysis of Cinnamoylvanillic Acid.—Cinnamoylvanillic acid (0.5 g.) was refluxed with 10% alcoholic potash (10 c.c.) for 2 hours and the reaction mixture was worked up in the usual manner. The residue yielded vanillic acid, yield 0.2 g., m.p. 205°, from hot chloroform solution. The mother-liquors on removal of chloroform and crystallisation from hot water gave cinnamic acid (0.2 g.), m.p. 132°.

1-*Tetra-acetylglucosido-4-cinnamoylvanillate* (I)

(1) *By Condensation of Cinnamoylvanillic Acid with Acetobromoglucose.*—Cinnamoylvanillic acid (2 g.), acetobromoglucose (4 g.) and dry silver oxide (4 g.) were mixed in dry quinoline (12 c.c.) in a conical flask and triturated for 15 minutes with occasional cooling under tap water till the paste turned into a semi-solid mass. The flask was left in a desiccator for 45 minutes and then glacial acetic acid (40 c.c.) was slowly added to it with cooling, and the resultant suspension centrifuged to remove the insoluble silver salts. The clear decantate was poured over crushed ice and the precipitated acetylglucoside filtered, dried and crystallised from hot alcohol, m.p. 158°, yield 3.3 g. (87%). $[\alpha]_D^{22} = -23.66°$ (1% chloroform solution). (Found: C, 59.2; H, 5.2. $C_{31}H_{32}O_{14}$ requires C, 59.2; H, 5.1 per cent).

(2) *By Condensation of Silver Salt of Cinnamoylvanillic Acid with Acetobromoglucose.*—Silver cinnamoylvanillate (1.1 g.) was suspended in dry xylene (50 c.c.) and half of the xylene was distilled to remove the traces of moisture in it. Acetobromoglucose (1.0 g.) was then added and the mixture heated under reflux for 4½ hours.

The precipitated silver salts were filtered hot and the filtrate concentrated under reduced pressure. Ether and petroleum ether were added to the concentrate to turbidity and the mixture was left in a refrigerator. The crystalline deposit of colorless needles was filtered and recrystallised from alcohol, m.p. 159°, yield 0.35 g. (22%). It does not depress the melting point of acetylglucosidocinnamoylvanillate, obtained by the procedure (1).

Hydrolysis of 1-Tetra-acetylglucosido-4-cinnamoylvanillate.—The acetylglucoside (42 mg.) was refluxed with 2% alcoholic caustic soda solution (1.5 c.c.) for 3 hours. The reaction mixture was neutralised and evaporated to dryness on a water-bath. The residue was extracted with ether and on usual working up it gave vanillic acid (8 mg.), m.p. 201°, and cinnamic acid (7.8 mg.), m p. 133°. The ether-insoluble residue was dissolved in 1 c.c. of water and yielded 11.5 mg. of glucosazone.

The results of paper chromatography of the hydrolysates are shown in Table I.

Action of Methanolic Ammonia on 1-Tetra-acetylglucosido-4-cinnamoylvanillate.—The acetylglucoside (1 g.) was suspended in methanol (20 c.c.) and saturated with dry ammonia at 0°. The clear solution was allowed to stand in a refrigerator for 12 hours and then freed of ammonia and the solvent in vacuo at 30°. On adding crushed ice to the straw-coloured residue, a colorless crystalline precipitate separated out. It was filtered off and recrystallised from hot water, m. p. 146°, yield 35 mg. [Found: C, 73.6; H, 6.1; N, 9.2; M. W. (Rast), 147. Calc. for C_9H_9ON: C, 73.4; H, 6.1; N, 9.5 per cent. M.W., 147].

It did not give any depression in melting point on admixture with an authentic sample of cinnamamide.

The aqueous filtrate was completely freed of the solvent in vacuo at 40° and ammonium acetate was removed from the residue by heating at 80°/3 mm. The straw-coloured residue was dissolved in absolute alcohol and left in the cold. After a few days a colorless deposit of needles was obtained, filtered and recrystallised from absolute alcohol, m.p. 207°, yield 85 mg. On drying at 100° in vacuo the m.p. rose to 224°. (Found: C, 50.99; H, 5.77. Calc.for $C_{14}H_{18}O_9$: C, 50.9; H, 5.75 per cent).

On admixture with an authentic sample of glucosidovanillate, prepared in the following manner, no depression in its melting point was observed.

1-Tetra-acetylglucosido-4-acetylvanillate (IV).—Acetylvanillic acid (1.0 g.), acetobromoglucose (3.6 g.) and dry silver oxide (4 g.) were reacted together in dry quinoline (15 c.c.) according to the procedure previously described. The precipitated glucoside was crystallised from hot alcohol as colorless needles, m.p. 160°, yield 0.85 g. $[\alpha]_D^{22} = -33.3°$ (1% $CHCl_3$ soln.). (Found: C, 52.8; H, 5.4. $C_{24}H_{28}O_{14}$ requires C, 53.3; H, 5.2 per cent).

1-β-D-Glucosidodvanillate (III).—The acetylglucoside (IV, 0.5 g.) was suspended in methanol (15 c.c.) and saturated with dry ammonia at 0°. The clear solution was kept in the cold for 12 hours and worked up in the manner outlined earlier. The final residue was dissolved in absolute alcohol and cooled. The crystalline deposit of the glucosidovanillate was filtered and recrystallised from the same solvent, m.p. 208°, yield 38 mg. On drying in vacuo at 100° the melting point rose to 222°. It was hydro-

lysed by emulsin and showed $[\alpha]_D^{22} = -125.3°$ in 1% aqueous solution. (Found : C, 50.6 H, 6.3. $C_{14}H_{18}O_9$ requires C, 50.9; H, 5.75 per cent).

Paper Chromatography oft he Hydrolysates of the above Glucosides

For Acids.—The hydrolysates were applied to a Whatman filter paper strip along with known spots of cinnamic, vanillic and cinnamoylvanillic acids and the paper was developed with butanol : ethanol : water : ammonia (*d* 0.88) (40 : 40 : 16 : 4) for 16 hours, dried at 80° for 15 minutes and the spots located by spraying BDH universal indicator adjusted to p_H 9-10 (Long, Quale and Stedman, *J. Chem. Soc.*, 1951, 2197).

For Glucose.—The paper was developed with butanol : ethanol : water (4 : 1 : 5) and the spots located with aniline hydrogen phthalate. The results are shown in Table I.

TABLE I

Substance.	Hydrolysing agent.	*Rf* values of products.
1. 1-Tetra-acetyl glucosido-4-cinnamoylvanillate	2% EtOH-KOH	0.73 (cinnamic acid) 0.32 (vanillic acid) 0.104 (glucose)
2. 1-Tetra-acetylglucosido-4-acetylvanillate	5% EtOH-HCl	0.35 (acetylvanillic acid) 0.104 (glucose)
3. 1-Glucosidovanillate	5% HCl	0.32 (vanillic acid) 0.105 (glucose)

The *Rf* value for cinnamoylvanillic acid = 0.80.

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